MODERN INORGANIC CHEMISTRY

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BY

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WITH ILLUSTRATIONS

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PREFACE

The true aim of the teacher must be to impart an appreciation of method, and not a knowledge of facts —K PEARSON

The power to recognize and to follow truth cannot be conferred by academical degrees —PARACELSUS

EVERY teacher now recognizes that it is a sheer waste of time to introduce many abstract ideas into an elementary science course without a previous survey of facts from which the generalizations can be derived In most cases the historical mode of treatment is correct, because the generalizations have usually been developed from a contemplation of the facts, in other cases the historical treatment may involve digressions which would seriously interfere with the efficiency of the course Obviously, a teacher will try his best to instil the maximum amount of scientific method into the facts—as prescribed by his syllabus and time table—always remembering that the student gets more lasting benefit from the method than from the facts *per se* In after life the scientific method may be retained as a permanent attitude of the mind when the facts themselves are nearly all forgotten Consequently, the teacher seeks to develop a certain spirit or attitude of mind which is almost equivalent to a sixth sense, and therefore the justification for a general course in chemistry must be sought in the mind of the student rather than in the facts of the science What, then, may a student expect from a general course of chemistry?

1 *Skill in observation and experiment*—All are agreed that personal contact with facts is a great advantage The constant absorption of statements and opinions from text books makes a student lean so much on authority that he ultimately becomes unfitted for independent observation Habits of self-reliance, resource, and initiative can be acquired only in the laboratory, or by direct contact with the facts themselves But practice in observation and experiment is not alone sufficient to develop the scientific faculty. The observational powers of a savage are usually keener than those

of a civilized man, and a student may learn to observe without gaining much beyond an increased facility in the art and he may become very skilful in experimenting without gaining much more than mere dexterity in manipulation

2 *Memory and knowledge of relevant facts.*—Facts, of course, form the raw material which is refined by scientific methods into science itself. Science can do nothing without facts. Consequently, many facts must be memorized by the neophyte in chemistry Some students soon learn the trick of amassing and memorizing all kinds of information in a mechanical way All the facts associated with a phenomenon may not be of equal importance In practice it is not always easy to discriminate between relevant and irrelevant facts Still, it is important to confine the attention as closely as possible to relevant and essential facts, and to discard those irrelevant and accidental The tyro in chemistry must trust his teacher to indicate the more significant facts to be committed to memory, and used as material for exercising his intellect and wits

3 *Ability to reason and think in a logical systematic way*—A student must learn to reflect on the available data bearing on the problem in hand, and to explain a phenomenon by drawing legitimate inferences from approved evidence It is a mistake to postpone the exercise and discipline of the thinking faculties until a student has memorized a vast accumulation of facts It is necessary to form habits of reflection and thought as early as possible Exercise means growth. It is far easier to acquire a mass of facts than to learn to draw a sound inference as to what the facts prove The thinking faculty can be developed only through the student's own individual efforts Just as the memory, in some subtle way, grows more vigorous with use, so the exercise of the thinking faculties enhances the power to think Every exercise of the reason, said Sir Humphrey Davy, in 1811, strengthens the habit of correct thinking, and adds sometimes to the influence and power of common sense Vague indefinite observing is usually followed by muddled inchoate thinking Clear thinking pre supposes clear seeing

4 *Cultivation of the imagination*—Some teachers have very pronounced objections to the introduction of scientific theories in an elementary course, they claim that "it is not scientific to present and discuss, say, the atomic theory in an elementary chemistry course" It might be asked what constitutes an elementary course? It would be a great mistake to suppose that science has no need for the imagination, for it is very true, as K Pearson has said, that

"disciplined imagination has been at the bottom of all great scientific discoveries" and, as W A Fiske has said, that "every hypothesis and law of science is the result of a vivid imagination" Imagination helps to complete the picture outlined by observation and inference The picture must, of course, be tested and criticized in every conceivable way to make sure that it is not a mirage among the purpled morning clouds to be dispelled by the dawning light

5 *Development of a critical and impartial judgment*—The imagination, though very useful, is a most dangerous ally, and a sharp line of demarcation must be observed between valid or legitimate deductions from the evidence, and what has been supplied by the imagination Each proposition must be judged solely on its merits There must be no shirking of the facts, no exaggeration, no distortion of the naked truth The mind must be kept open and free from prejudice The student must learn not to prejudge data and phenomena by ideas formed independently of the things themselves A teacher soon accumulates remarkable examples of the influence of expectation on judgment If a practical class knows what quantitative result "ought" to be obtained, it is surprising how much nearer that result the majority will get than if the true result were unknown—and this without dishonest intentions Rigorous honesty and absolute impartiality in dealing with approved evidence are indispensable A complete absence of bias can alone give reality and meaning to scientific truths

I have to thank several authorities for permission to use a number of quotations and a selection of questions from college examination papers The source of each is indicated in the text The original wording of the examination questions has been slightly modified in a very few cases I have pleasure in thanking a number of friends for reading portions of the proofs In some cases I have persuaded friends who have specially studied a particular phenomenon or process to glance through the proofs to make sure all is sound I gratefully acknowledge the help I have consciously and sub consciously received from the examination and review of a large number of text-books during the past few years Messrs A D Holdcroft and J. C Green have kindly read through the proofs, and I am very grateful for their help I am also indebted to Mr F J Austin for the photography

J W. M.

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MODERN INORGANIC CHEMISTRY

CHAPTER I

INTRODUCTION

§ 1 Observation and Record Collecting Data.

> To what can we refer for knowledge? What can be a more certain criterion than the senses themselves? If we cannot trust the senses, how is it possible to distinguish what is true from what is false?—LUCRETIUS

IN ancient times the majority of educated people believed it to be undignified for a self-respecting man to make experiments, and they did not consider knowledge obtained by observing nature to be a serious subject worthy of mental occupation Accordingly, the leading philosophers devoted themselves to fantastic and chimerical hypotheses about material things, and made no earnest attempt to discriminate between the unreal and the real, in consequence, their minds became so prejudiced that facts were either denied or else explained by extravagant ideas and fancies uncontrolled by truth and reality as we understand these terms to day

True knowledge about material things can be obtained only through the senses, there is no other way Experience is the well spring of true knowledge, experience alone can teach something new; it alone is irrefutable, it alone can give certainty Experience comprises all the impressions we observe and perceive through the various organs of sense These impressions are recorded in our notebooks, dictionaries of chemistry, etc, as empirical facts The facts make the ground upon which science is built. The edifice can only be stable in so far as it is founded upon the immutability of facts The facts must be accurate, or the edifice will be unstable

Not many years ago, an apt quotation from one of the classical writers —say Aristotle—was considered ample proof of the truth of any statement, to day, science looks askance on records of mere opinions, and focuses its attention on records of facts It is not always easy to record facts faithfully without unconscious distortion, or bias Things are not always what they seem It is often difficult to distinguish appearances from realities The sun appears to rise and set, in reality, it does neither As Robert Hooke would have said: it is necessary to be on guard against

deep rooted errors which may have been grafted upon science by the slipperiness of memory, the narrowness of the senses, and the rashness of the understanding The greatest caution must be exercised in accepting on second hand evidence, facts which cannot be verified. No reliance can be placed on vague impressions. Evidence must be clear and precise

Few persons can estimate and register facts impartially and fairly As W S Jevons puts it "Among uncultured observers, the tendency to remark favourable, and forget unfavourable, events is so great that no reliance can be placed upon their supposed observations" The student must therefore spare no pains to acquire the habit of recording phenomena just as they are observed, and of distinguishing sharply between what is, or what has been, actually seen, and what is mentally supplied Above all, said Robert Hooke (1665), a good observer needs a sincere hand and a faithful eye, to examine and record the things themselves as they really appear

§ 2 The Correlation of Observations Classifying Data

> In order that the facts obtained by observation and experiment may be capable of being used in furtherance of our exact and solid knowledge, they must be apprehended and analyzed according to some conceptions which, applied for this purpose, give distinct and definite results, such as can be steadily taken hold of, and reasoned from —W WHEWELL.

The record of facts obtained by observation and experiment, *per se*, is empirical knowledge. Nature presents to our senses a panorama of phenomena co mingled in endless variety, so that we are sometimes overwhelmed and dazed by the apparent complexity of empirical knowledge It is the work for the intellect to educe the elements of sameness amidst apparent diversity, and to see differences amidst apparent identity. It is work for the judgment to reject accidental and transient attributes, and to consolidate essential and abiding qualities

Empirical knowledge must therefore be arranged, re-arranged, grouped, and classified so as to emphasize the elements of similarity and identity in different phenomena This means that the facts must be arranged in a methodical and systematic manner so that finally all the facts taken together may form one system The process of classification and correlation is one of the methods of scientific investigation—*the deductive method* Knowledge so systematized is scientific knowledge

To take a particular case, the material framework of the world appears in a myriad different guises and combinations but the chemist can resolve each combination into a few definite elementary forms of matter, similarly, a "multitude of forces" can be resolved into comparatively a few primitive forms of energy As the student grows in scientific knowledge, he will find in chemistry a curious mixture of both empirical and scientific knowledge

§ 3 The Generalization of Observations

> It is the intuition of unity amid diversity which impels the mind to form a science —F S HOFFMAN

The correlation of empirical facts requires qualities of the mind different from those employed in observation and experiment Both qualities are not always located in the same individual Some excel in the one, not

in the other. Priestley and Scheele, for instance, were admirable observers, but they were not brilliant in the work of correlation; Dalton and Lavoisier were not particularly distinguished as experimenters, but they excelled in correlating experimental data.

There is still a higher type of work for but a few seekers after knowledge. It is—

> To search thro' all
> And reach the law within the law.—Tennyson.

Particular groups of facts must be unified or generalized into a system—the so-called law. As I have pointed out elsewhere, Newton's celebrated law epitomizes in one simple statement how bodies have always been observed to fall in the past. Newton did not discover the cause of the falling of the apple, but he did show that it was due to the operation of the same forces which hold the earth, the planets, and their satellites in their appropriate orbits. The scientific generalization explains the operations of nature by showing the elements of sameness in what at first sight appears to be a confused jumble of phenomena. Generalization is the golden thread which binds many facts into one simple description. The rare quality of mind required for the work of generalization is found only in a Newton and in a Darwin. Plato said that if ever he found a man who could detect the *one in many*, he would follow him as a god.

§ 4 The Aim of Science in general, and of Chemistry in particular.

> Let us remember please that the search for the constitution of the world is one of the greatest and noblest problems presented by nature.—G. Galilei.

Science embraces the sum-total of human knowledge and it ranges over the whole realm of nature. Science is not a mass of empirical knowledge gained by observation and experiment, but it is an organized body of facts which have been co-ordinated and generalized into a system. Science tacitly assumes that nature is a harmonious unity. Science seeks a complete knowledge of the multitude of inter-related parts of the universe which act and react on one another producing endless diversity. In fine, science aims at omniscience. The target, however, appears to recede with increasing knowledge, and science might well confess with Tennyson—

> So runs my dream; But what am I?
> An infant crying in the night;
> An infant crying for the light;
> And with no language but a cry.

Our feeble wit has rendered it necessary to rear a tree of scientific knowledge with many branches: astronomy, physics, chemistry, mineralogy, geology, biology, sociology, etc. "The divisions of the sciences," said Francis Bacon, "are like the branches of a tree that join in one trunk," and they are, therefore, more or less closely related one with another. The astronomer, the physicist, the chemist, each usually keeps to his own particular branch.

The science of chemistry is man's attempt[1] to classify his

[1] "Is it necessary to the nature of a science that it be all true, and that it contains no admixture of error?" asked S. Brown in 1849. The answer is: By no means! Otherwise chemistry was no science during the reign of phlogiston;

knowledge of all the different kinds of matter in the universe, of the ultimate constitution of matter, and of the phenomena which occur when the different kinds of matter react one with another The science of chemistry is itself so vast that many branchlets are necessary for useful work, and thus we have inorganic chemistry, organic chemistry, physical chemistry, mineralogical chemistry, bio chemistry, agricultural chemistry, metallurgy, etc The chemist also frequently aims at applying his knowledge to useful purposes in the arts and industries, thus arises applied, industrial, or technical chemistry

§ 5 Experiment.

> Experiment is the interpreter of nature Experiments never deceive It is our judgment which sometimes deceives itself because it expects results which experiment refuses We must consult experiment, varying the circumstances, until we have deduced general rules, for experiment alone can furnish reliable rules —LEONARDO DA VINCI

Chemistry is largely an experimental science The chemist would not make much progress if it were only possible to observe phenomena just as they occur in nature, and not possible to make observations under determinate conditions By experiment, it is possible to make combinations of different forces, and different forms of matter which are not known to occur in nature Every experiment has the character of a specific question The skilled experimenter knows what he is asking, and he tries his best to interpret nature's reply, be it affirmative, negative, or evasive.

Natural phenomena, *per se*, are usually too complex for our minds to grapple Phenomena must be simplified by simple experiments This idea was in R Hooke's mind when he said "The footsteps of nature are to be traced, not only in her ordinary course, but when she seems to be put to her shifts, to make doublings and turnings, and to use some kind of art in endeavouring to avoid our discovery" The more intricate the experiment, the greater the probability of an obscure and ambiguous result As Lavoisier has pointed out, "it is a necessary principle in experimental work to eliminate every complication, and to make the experiments as simple as possible"

Joseph Priestley believed in making a large number of haphazard experiments, and he discovered oxygen by trying the effect of heat on "many substances," apparently selected at random by John Warltire of Birmingham Thomas A Edison, also, appears to have discovered the phosphorescence of calcium tungstate when exposed to Röntgen's rays by deliberately trying the effect of these rays on a large collection of different substances This old prosaic method of experimenting by "trying everything" is necessary in some cases, and, though usually dubbed "empirical" or "rule of thumb," the process is fundamentally scientific,[1] but it is not

and the Lavoisierian chemistry no science as long as oxygen was taken for the principle of acidity Indeed, the chemistry of to day could very easily be proved to be not science, if "man's attempt" were to be rejected unless it can be proved to be "the whole truth and nothing but the truth"

[1] Empirical is derived from a Greek word meaning experience It has been emphasized in the text that all knowledge is derived from experience, and hence empiricism would appear to be the right method of acquiring knowledge The term however has slightly changed in meaning for it is now usually applied to chance experiences which occur irregularly without any orderly plan of investigation

usually economical in time and labour. Discoveries are then due, as Priestley believed, more to "chance than to any proper design or preconceived theory." More frequently the track of the experimenter is blazed by means of working hypotheses.

§ 6 Hypothesis, Theory, and Law

> We are gifted with the power of imagination, and by this power we can enlighten the darkness which surrounds the world of the senses Bounded and conditioned by co-operant reason, imagination becomes the mightiest instrument of the physical discoverer —J TYNDALL

It is a popular belief that "the aim of science is to explain things" As just indicated the so-called explanations of science do not usually get much beyond describing the observed facts in the simplest possible terms The description may emphasize the history of a phenomenon or the conditions under which a phenomenon occurs, in other words, science may explain a phenomenon by describing how one event is determined by an antecedent event—sometimes called a cause, and how one particular set of conditions—the cause or causes—can give rise to another set of conditions—the event, but owing to the limitation of man's understanding, we are far, very far, from comprehending the true relations and the true causes of natural phenomena In consequence, we are compelled to build an imaginary model showing how a given set of conditions—the hypothesis—can produce a particular event A phenomenon is then explained by showing that it would be bound to occur by the operation of the set of conditions postulated by the hypothesis. Consequently, hypotheses are essentially guesses at truth.

Hypotheses precede observation and prompt experiments Hence, when Leonardo da Vinci (c 1500) said that "hypothesis is the general, and experiments are the soldiers," he probably meant that hypotheses direct or indicate what experiments should be made Accordingly, hypotheses are indispensable aids in the systematic quest after the secret meaning in nature's deeds An hypothesis may seem to be the logical consequence of known facts, or it may be a random flash of the imagination However probable an hypothesis might appear, both the hypothesis and the logical consequences of the hypothesis must be tested by comparison with facts It is not wise to dogmatize when direct trial is possible, it is so easy to err—by ignorance or oversight—that even when a conclusion appears to be indisputably connected with known facts, the test must be applied. If one hypothesis does not fit the facts, it is discarded, and a modification of the old, or a totally new hypothesis is tried "To try wrong guesses is apparently the only way to hit the right ones" This method of "trial and failure" is continued until a successful guess crowns the investigation, but one single real conflict between fact and hypothesis will destroy the most plausible hypothesis Quoting M. Faraday "The world little knows how many of the thoughts and theories which have passed through the mind of an investigator have been crushed in silence and secrecy by his own severe criticism and adverse examination, that in the most successful instances not a tenth of the suggestions, the hopes, the wishes, and the preliminary conclusions have been realized"

An hypothesis contains a speculative term, an assumption which goes *beyond* the observed facts, while a law is a generalization which does not extend beyond the observed facts. A law is thus limited by the facts it describes. When an hypothesis has been so extended that it has a wide and comprehensive scope, the hypothesis becomes a theory. Like the hypothesis, a theory usually contains an "unproved assumption"—*e g* the kinetic theory, the atomic theory, etc.[1]

Two or more contradictory hypotheses may be consistent with the facts, both cannot be right. There is, then, need for an *experimentum crucis*—an experiment which will decide in favour of one, and exclude the other. An hypothesis is supposed to be established when it, and it alone, is in harmony with known facts. The hypothesis then ranks as a theory or law. Laws, theories, and hypotheses are all on probation. However successful a theory or law may have been in the past, directly it fails to interpret new discoveries, its work is finished, and it must be discarded or modified. On account of the "unproved assumption" embodied in all hypotheses, they are of necessity transient, fleeting, and less stable than theories, and theories, in turn, are less stable than laws. A theory believed to-day may be abandoned to-morrow. Hypotheses and theories are continually changing. Science in making is "a battle-field of competing theories," the path of progress is strewn with dying and dead hypotheses.

The student will now recognize two important methods of scientific investigation.

1. *Bacon's deductive method*.—Here the facts are collected, and exhaustively classified until the generalization becomes clear. The method proceeds *a particulari ad universale*.

2. *Newton's inductive method*.—Provisional generalizations, called "hypotheses," or "working hypotheses," are devised to explain phenomena. Observation and experiment are afterwards employed to test the validity of the proposed generalization.

Summary. According to Bacon, facts are used to make theories *from*, and according to Newton, to try ready made theories *by*. In order to illustrate how the inductive method is employed in scientific investigation, let us try to find an hypothesis to explain why certain metals increase in weight when calcined in air. Several other important examples will be given later, for instance, "Lavoisier's experiments on the transformation of water into earth", "Mayow's work on combustion", "the phlogiston hypothesis," etc. Newton's phrase *hypotheses non fingo* (I do not frame hypotheses) is often quoted to show that he discountenanced the inductive method of scientific investigation. This is based on a misunderstanding, for Newton, on the contrary, asserted that "no great discovery was ever made without a bold guess."

[1] Some writers—*e g* W. Ostwald—apply the term "theory" to a generalization which does not extend beyond the observed facts, and in that case "theory" becomes "law" when the generalization has a wide and comprehensive scope. There are thus, at least, two distinct uses of the term "theory". For historical reasons the terms may appear to be confused because the passage of "hypothesis" to "theory," or of "theory" to "law" has not always been attended by a change of the corresponding terms—*e.g* Avogadro's "hypothesis," by the definitions in the text might be called a "theory".

§ 7 Rey's Experiments on the Calcination of Metals in Air

Let all the greatest minds in the world be fused into one mind, and let this great mind strain every nerve beyond its power; let it seek diligently on the earth and in the heavens; let it search every nook and cranny of nature; it will only find the cause of the increased weight of the calcined metal in the air —JEAN REY (1630)

As early as the eighth century, the Arabian chemist Yeber-Abou-Moussah-Djafer Al-Sofi, commonly called Geber,[1] knew that when metallic lead is calcined in air, the resulting calx is heavier than the original metal[2] The increase in weight seems to have surprised and puzzled the earlier chemists The result was, later on, said to be due to "the absorption of the vapours of charcoal," or, as R Boyle (1683) expressed it, to "the arresting of igneous corpuscles" which passed through the walls of the vessel in which the metal was calcined, or to "the removal of matter from the calcining vessel" These hypotheses, more or less modified, were in vogue for nearly a century Jean Rey (1630) appears to have been the first to test the hypotheses by an appeal to experiment

1 The facts —In order to clarify the mind, let us review the facts. Four things are present during the calcination of the metal in air (1) The containing vessel or crucible, (2) The metal being calcined, (3) The air, and (4) The source of heat. Again the metal and the containing vessel weigh more after the calcination than they did before.

2 The hypotheses —In applying the inductive method of investigation to these facts, *it is necessary to review every rational explanation consistent with the facts, and to examine each hypothesis impartially,* since, as emphasized above, it is necessary to show that the explanation finally selected is *alone* consistent with the facts This extension of the inductive process might be called the method of exhaustion It is a mistake to confine the attention to one hypothesis, because that might seriously limit the range of the inquiry The mind unconsciously assimilates evidence in favour of a pet hypothesis, and a pet hypothesis is apt to grow from a favoured child to a tyrannical master Four plausible hypotheses may be suggested to explain the cause of the increase in weight (1) the gases, etc, from the source of heat unite with the containing vessel, (2) the air unites with the containing vessel, (3) the gases from the flame penetrate the crucible, and unite with the metal, and (4) the air unites with the metal[3]

[1] Many discoveries are attributed to Geber (died 777) which appear to have wrongfully crept into the Latin translations of his writings, for instance, the discovery of sulphuric acid is generally attributed to Geber, although E Lippmann (1901) has stated that sulphuric acid was not known to the Arabian writers prior to 975 A D Many consider "Geber" to be a mythical personage

[2] The process of heating a metal in air so as to convert it into a calx, is called *calcination* The calces are generally equivalent to what the modern chemist calls "metallic oxides"

[3] The phlogiston theory—that on calcination metals lose a hypothetical substance called *phlogiston*—is discussed later According to G E Stahl (1723), "the fact that metals, when transformed into their calces, increase in weight does not disprove the phlogiston theory, but, on the contrary, confirms it, because phlogiston is lighter than air, and, in combining with substances, strives to lift them, and so decreases their weight, consequently, a substance which has lost phlogiston must be heavier" It may not seem rational to postulate the existence of a substance weighing less than nothing It will be observed, however, that the assertion

3 Testing the hypotheses by experiment —By heating the crucible alone, without the metal, no change in weight occurs This "blank," "dummy," or "control" experiment shows that neither the first nor the second hypothesis will account for the increase in weight of the metal The third hypothesis can be tested by heating the crucible and the metal out of contact with the air There is then no change in the weight of the metal The third hypothesis is therefore untenable This method was not practicable for the early chemists, and hence Rey employed a less decisive test It might be expected that if the results depend upon the absorption of the flame gases, different results must be obtained by using different sources of heat—sun glass, etc.—but the same results are obtained in every case, and accordingly the third hypothesis is probably wrong

4 The conclusion —Apparently the only constant factor is air *The sole invariable antecedent of a phenomenon is probably its cause* Hence, unless something has been overlooked, we conclude that when metals are heated in air, the increase in weight is due to the fixation of air by the metal, and not to the absorption of furnace gases, nor to variations in the weight of the vessel in which the calcination is made

Rey also made the interesting unforeseen observation that "nature, in her inscrutable wisdom, has set limits which she does not overstep", in other words, *however long a metal may be heated in air, a definite weight of each metal can combine with only a definite maximum amount of air* Students to day regularly repeat Rey's experiments on the metals—under various guises—as class exercises The following table is taken from students' laboratory notebooks —

TABLE I —ACTION OF AIR ON THE CALCINATION OF THE METALS

Metal	Weight of metal Gram	Weight of calx Gram	Increase in weight Gram	Ratio Weight air absorbed Metal used
Magnesium	1	1 658	0·658	1 1 52
Zinc	1	1 246	0 246	1 4 06
Aluminium	1	1 890	0 890	1 1 12
Copper	1	1 252	0 252	1 3 97
Tin	1	1 269	0 269	1 3 72

Hence, one gram of the absorbed air is respectively equivalent to

(Absorbed air)	Magnesium	Zinc	Aluminium	Copper	Tin
1	1 52	4 06	1 12	3 97	3 72 grms.

5 Anticipation of new phenomena —A good hypothesis ought to predict phenomena which have not been observed, and to foretell the results of new experiments, because, if the hypothesis be true, it ought

all matter is heavy and possesses weight, is only one way of saying that "the attraction of gravitation exists between all masses of matter" This is by no means a self evident principle because it is just as easy to conceive of two masses of matter repelling one another, and easier still to conceive of two masses of matter neither attracting nor repelling one another Hence, the assumption of a phlogiston weighing less than nothing is not so silly as is sometimes supposed It is quite true that such forms of matter have never been detected, and, accordingly, we assume that they do not exist Hence also arises the definition of matter indicated in a later chapter

to include all other cases A hypothesis which is not illogical and which does not contradict known facts is to be judged by its usefulness The end justifies the means [1] When the consequences of a hypothesis are logically deduced, a good hypothesis should not only explain, but it should also anticipate facts Rey's hypothesis can be used to predict new results. In 1770, A L Lavoisier wrote

> Thus did I at the beginning reason with myself If the increase in weight of a metal calx (calcined in a closed vessel) be not due to the addition of fire matter, nor of any other extraneous matter, but to the fixation of a portion of the air contained in the vessel, the whole vessel after calcination, must be no heavier than before, and must merely be partly void of air, and the increase in the weight of the vessel will not occur until after the air required has entered

Lavoisier confirmed this inference experimentally on November 12, 1774, although the gifted Russian chemist, M. W. Lomonossoff had come to the same conclusion in 1756, eighteen years before Lavoisier.

§ 8 Lavoisier's Experiments on the Composition of Air.

> Nature is ever making signs to us, she is ever whispering to us the beginnings of her secrets, the scientific man must be ever on the watch, ready at once to lay hold of nature's hint, however small, to listen to her whisper however low —M Foster

Antoine Laurent Lavoisier (1774) extended Rey's experiments with more decisive results. Lavoisier heated tin along with air in a *closed* vessel The vessel containing the air and tin did not increase in weight, although part of the air was absorbed. When the flask was opened, air rushed in, and the increase in the weight of the vessel was found to be equal to the increase in weight which the tin alone had suffered. Hence, Lavoisier concluded, with Rey, that the increase in the weight of the tin was solely due to an absorption of the air in which the calcination had occurred. There was not sufficient air in the flask to "saturate" all the tin, and yet some air always remained as a residue Hence, Lavoisier concluded further that only part of the air can combine with the metal during the calcination; he also found that *the increase in the weight of the tin during calcination is equal to the decrease in the weight of the air.* Hence, it seems as if air contains at least two constituents, only one of which is absorbed by the heated metal This inference must be tested by experiment

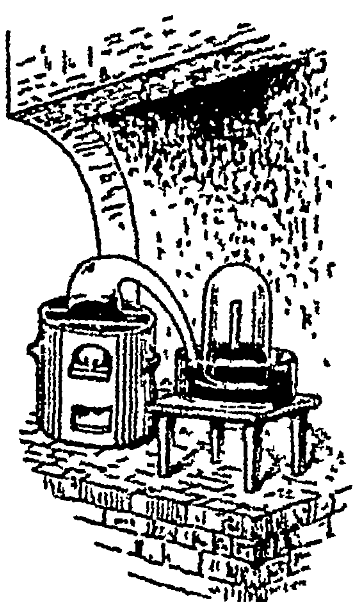

FIG 1 —Lavoisier's experiment on the Composition of Air

Lavoisier continued this important work with mercury instead of tin. The mercury was confined in a retort with an S shaped neck which dipped under a bell jar in a trough of mercury, as illustrated in Fig 1. The air

[1] G J Stoney expressed the idea neatly "A theory is a supposition we hope to be true, a hypothesis is a supposition which we expect to be useful."

in the retort was in communication with the air in the bell jar The level of the mercury in the bell jar was adjusted at a convenient level, and its position "very carefully marked with a strip of gummed paper" By means of a charcoal furnace, the mercury in the retort was heated—not quite to its boiling point Lavoisier said "Nothing of note occurred during the first day The second day I saw little red particles [1] swimming over the surface of the mercury, and these increased in number and volume during four or five days, they then stopped increasing and remained in the same condition At the expiration of twelve days, seeing that the calcination of the mercury made no further progress, I put the fire out." After making allowance for variations of temperature and pressure, Lavoisier noticed that the volume of air in contact with the mercury was about 50 cubic "inches," and after the experiment, between 42 and 43 cubic "inches" About one sixth of the volume of air in the apparatus was absorbed by the mercury [2] The air which remained in the retort was not absorbed by the hot mercury, it extinguished the flame of a burning candle immersed in the gas, [3] and a mouse was quickly suffocated when placed in the gas Hence, Lavoisier called the gas azote, "from the ἀ privative of the Greeks, and ζωή, life" In France the gas is still "azote," though in Britain it is called "nitrogen," and in Germany "Stickstoff," that is, "suffocating stuff"

By collecting the red powder and reheating it in a suitable retort, Lavoisier obtained between 7 and 8 cubic "inches" of a gas which had obviously been previously removed from the air by the hot mercury When a burning candle was immersed in the gas, the candle burnt with "blinding brilliancy," as Lavoisier expressed it, a smouldering splinter of wood burst into flame when plunged in the gas, and the gas did not suffocate a mouse like azote Lavoisier first called this gas *vital air*, and afterwards *oxygen* The latter term is its present day designation In this manner, Lavoisier proved that atmospheric air is made up of two gases—oxygen and nitrogen—of different and even opposite natures,[4] the oxygen alone combines with the metal during calcination

Assuming that this interpretation of the experiments is correct, Lavoisier inferred that by mixing azote and oxygen in the right proportions, it ought to be possible to reproduce atmospheric air This Lavoisier did, and the mixture was found to behave with respect to "combustion, respiration, and the calcination of metals similar in every respect to atmospheric air"

Joseph Black (1778) showed that atmospheric air contained a small

[1] The calx or oxide of mercury is red It is now called "red oxide of mercury," or "mercuric oxide"

[2] More exact experiments show that one fifth would be nearer the mark.

[3] The old chemists used the term *air* where we use *gas* in the sense of an aëriform elastic fluid John Baptista van Helmont (*Oriatrike, or Physick Refined*, posthumous Eng trans London, 1662), introduced the word *gas* into chemistry in order to distinguish the vapour given off by water at ordinary temperatures from steam He said the term "*gas* is not far severed from the *chaos* of the auntients" (ancients) Just as the "chaos of the auntients" was a confused mixture of elements from which the Creator produced the universe, so, to Van Helmont, the vapour of water was a confused mass of elements from which all material substances could be produced It is an easy transition from *chaos* to *chas*, which has the sound of *gas*—G F Rodwell Some derive the word *gas* from the *geist* (spirit) of the Germans

[4] It must be added that K W Scheele (1777) was about the first to state definitely that air "must be made up of two kinds of elastic fluids" (gases)

unknown, the fact would be important and it would change the face of chemistry, but it would not render useless any facts we know about chlorine.

The old alchemists sought to transform some of the common metals into gold. Whenever the attempt has been made with materials known to be free from gold, no transmutation has been observed. There is nothing intrinsically absurd in the notion, but at present, no authentic transmutation has been deliberately, or rather intentionally, accomplished. When the evidence has permitted a critical examination, every recorded instance has been traced to a mal-observation[1]; and evidence which cannot be tested is outside the range of scientific methods.

§ 10 The Four-Element Theory.

Four elements intimately united
Form the whole world.—SCHILLER.

The four element theory is one of the oldest attempts to classify the multitudinous forms of matter which make up the world. To the early philosophers, the world was composed of four distinct principles or entities—the *earth* typified all solids; *water*, liquids; *air*, the winds, clouds, and the breath; and lastly *fire* which was the symbol of the sun, and worshipped by many as a god. Hence, in the writings of the alchemists, we usually find a chapter devoted to this quartet: earth, water, air, and fire. The early philosophers added a fifth element—*quinta essentia*—perhaps analogous with the primal matter of the Greeks. This was supposed to be a subtle extract, the quintessence of the other four. The ancient Hindu philosophers had previously added a fifth element which, in their system, was supposed to be the medium for propagating sound, etc., and which, in consequence, had something in common with the modern concept of an æther pervading all space.[2]

The four-element theory was demolished when water, air, and the earths were decomposed into still simpler bodies; and when fire was shown to be a manifestation of energy. It is probable that the term "element" was not used by the old philosophers in the same sense that it is to-day. Whatever the idea involved in the four element theory, it was believed by many different races in different parts of the globe; it has pervaded the philosophy of all thinking races; it has been sung by the poets of every land; and it has had a longer life than any succeeding philosophy. The theory was living a couple of centuries ago; it is now dead.

[1] See the chapter on "Radioactivity" towards the end of this work.
[2] Air, not the æther, is the medium for propagating sound.

CHAPTER II

COMBINATION BY WEIGHT

§ 1 The Law of Constant Composition.

Nature in her unscrutable wisdom has set limits which she never oversteps —JEAN REY

ATTENTION must now be directed to the singular observation made by Jean Rey (1630) that during the calcination of a metal in air "the weight of the metal increased from the beginning to the end, but when the metal is saturated, it can take up no more air Do not continue the calcination in this hope you would lose your labour" The examples previously quoted—Table I—have shown that one gram, and only one gram, of air is absorbed by *definite amounts of the given metals* under the conditions of the experiment, and Lavoisier's work proves that the *oxygen* of the air is alone absorbed. Accordingly, one part by weight of oxygen is equivalent to

Oxygen	Magnesium.	Zinc.	Aluminium.	Copper	Tin.
1	1 52	4·06	1 12	3·97	3 72

Instead of taking the weight of oxygen unity, it will be more convenient, later on, and also more in accord with general usage, to make oxygen 8 instead of unity Hence, multiplying the preceding numbers by 8, we obtain

Oxygen.	Magnesium.	Zinc.	Aluminium	Copper	Tin
8	12 16	32 48	8 96	31 76	29 76

When magnesium is calcined in the presence of oxygen, or air, the metal always unites with the oxygen in the proportion of one part of oxygen per 1 52 parts of magnesium, or 8 parts by weight of oxygen per 12 16 parts by weight of magnesium The same principle obtains when magnesium oxide is made in several different ways, and likewise with the other metallic oxides Hence, as P G Hartog puts it two like portions of matter have the same composition. The converse of this statement is not necessarily true

The exact work of J S Stas and of T W Richards and many others has firmly established this deduction for the regular type of chemical compounds J S Stas (1860), for example, studied among other things, the composition of silver chloride prepared by four different processes at different temperatures He found that 100 parts of silver furnished 132 8425, 132 8475, 132 842, 132 848 parts of silver chloride, and that neither the temperature nor the method of preparation had any influence

on the composition of the chloride The difference between the two extremes is less than 0 006 part per 100 parts of silver This shows that the errors, incidental to all experimental work, are here remarkably small Hence, Stas stated "If the recognized constancy of stable chemical compounds needed further demonstration, I consider the almost absolute identity of my results has now completely proved it"

The student will take notice that *we are unable to prove the law of constant proportions with mathematical exactness However skilful a chemist may be, it is impossible to make an exact measurement without committing an "error of observation" or an "error of experiment"* It is assumed that the small difference 0 005 per cent between the two extreme results of Stas (1) is wholly due to the unavoidable errors of experiment, for we cannot expect an exact solution of the problem, and (2) is not due to a very slight inexactitude in the law of constant proportions. (*Cf* p 473)

The composition of a definite chemical compound appears to be independent of its mode of formation, and therefore it is inferred that substances always combine in definite proportions If an excess of one substance be present, the amount in excess is extraneous matter This deduction from the observed facts is called the law of definite proportions, or the law of constant composition a particular chemical compound always contains the same elements united together in the same proportions Probably no generalization in chemistry is more firmly established than this It was not discovered by any particular man, but gradually grew among the doctrines of chemistry The law was tacitly accepted by many before it was overtly enunciated—*e g* J Rey (1630), I. Newton (1706), G E Stahl (1720), F G Rouelle (1764), C F. Wenzel (1777), T Bergmann (1783), etc So great is the faith of chemists in the truth of this generalization that a few accurate and careful experiments are considered sufficient to settle, once for all the composition of a substance For instance, if a substance possessing all the properties of magnesium oxide be given to a chemist, without taking any more trouble, he knows that it will contain 12 16 parts of magnesium for every 8 parts of oxygen

Historical —The validity of the law was the subject of an interesting controversy during the years between 1800 and 1808 J L. Proust maintained that constant composition is the invariable rule, C L Berthollet maintained that constant composition is the exception, variable composition the rule Proust's words are worth quoting

According to my view, a compound is a privileged product to which nature has assigned a fixed composition Nature never produces a compound, even through the agency of man, other than balance in hand, *pondere et mensura*, Between pole and pole compounds are identical in composition Their appearance may vary owing to their manner of aggregation, but their properties never No differences have yet been observed between the oxides of iron from the South, and those from the North, the cinnabar of Japan has the same composition as the cinnabar of Spain, silver chloride is identically the same whether obtained from Peru or from Siberia, in all the world there is but one sodium chloride, one saltpetre, one calcium sulphate; and one barium sulphate Analysis confirms these facts at every step

It might be thought that positive assertions of this kind, backed by accurate experimental work, would leave no subject for disputation. But,

surveying the battlefield in the light of the present-day knowledge, it seems that another quite different phenomenon was confused with the law of constant composition, and the methods of analysis were not very precise. Some, probably from the unfounded belief that "Proust deservedly annihilated Berthollet," call the generalization discussed in this chapter, "Proust's law." We shall see later that a phenomenon which Proust apparently did not clearly recognize prevented him from annihilating Berthollet.

§ 2 Physical and Chemical Changes

One element or compound is distinguished from all other elements or compounds in possessing certain specific and characteristic properties. First and foremost, a chemical compound has a fixed and definite composition; then again, it melts and boils at definite temperatures; its specific gravity, specific heat, colour, odour, behaviour when in contact with other substances, etc., are characteristic of one particular chemical compound. When the melting point of, say, pure silver chloride has been once accurately determined, it follows that all other samples of pure silver chloride will melt at the same temperature under the same conditions. The more salient characteristic properties of an element or compound are employed as tests for its identification—that is, for distinguishing it from all other known compounds. Thus a student would be probably correct in stating that a solution contained a silver compound if it gave a white precipitate when acidified with hydrochloric acid, and the precipitate was insoluble in hot water, and soluble in aqueous ammonia.

Physical changes.—When liquid water becomes ice or steam there is no change in the *chemical* nature of the substance, for the matter which makes steam and ice is the same in kind as that of liquid water. A substance can generally change its state, as when liquid water becomes steam or ice. The idea is further emphasized by the fact that in most cases a substance is called by the same name, whether it be in the solid, liquid, or gaseous state of aggregation, *e.g.*, we speak of "liquid" oxygen, "liquid" air, "molten" silver chloride, etc. Again, matter may change its *volume* by expansion or contraction; it may change its *texture*, as when a porous solid is compressed to a compact mass; it may change its *form*, as when matter in bulk is ground to powder; it may change its *magnetic qualities*, as when a piece of soft iron in contact with a magnet attracts other pieces of iron, etc. It is conventionally[1] agreed to say that in none of these cases of physical change is there any evidence of the formation of a new substance, and that the matter does not lose or change those properties which distinguish it from other forms of matter. **A physical change involves an alteration in the properties of a substance without the formation of a new substance.**

[1] I must confess that in writing this book I have found this chapter to be the most difficult. We have some uncomfortable doubts if magnetized and demagnetized iron can be called the same kind of matter; similar remarks apply to say monoclinic and rhombic sulphur, and to water at −20°, +20°, and +120°. The student will appreciate the difficulty after reading § 3 in the chapter on "Water" and § 7 in the chapter on "Sulphur."

Chemical changes.—When magnesium metal is heated in air, a white powder is formed, and when mercuric oxide is similarly treated, mercury and oxygen are obtained. The action of heat in both cases furnishes forms of matter with very different specific properties from those forms of matter employed at the start. **A chemical change involves the formation of a fresh substance or substances, with different specific properties from the original substance or substances.** In both chemical and physical changes, as we shall soon find, the total mass of matter before and after the change remains constant, but in chemical changes alone the *kind* of matter alters.

It is not always easy to distinguish between physical and chemical changes, because the only real distinction between the two turns on the question: Is there any evidence of the formation of a new substance during the change? The evidence, as we shall soon see, is not always conclusive.

§ 3 Compounds and Mixtures.

1. **The constituents of a compound are combined in definite proportions.**—The law of constant proportions is of fundamental importance in forming a conception of the meaning of the term "chemical compound." If a substance produced in different ways be not constant in composition, it is not considered to be a chemical compound, but rather a mixture. R. Bunsen (1846), for example, showed that the proportion of oxygen to nitrogen in atmospheric air is not constant, because the oxygen varies from 20.97 to 20.84 per cent by volume, by methods of measurement with an error not exceeding 0.03 per cent. Hence, the oxygen and nitrogen in atmospheric air are said to be simply mixed together, and not combined chemically. We shall soon see, however, that substances with a definite composition are usually, but not always, chemical compounds.

Fig. 2.—Cornish Granite (× 50).

2. **Compounds are homogeneous, mixtures are usually heterogeneous.**—It is comparatively easy to detect particles of sugar and sand in a mixture of the two; and a simple inspection of a piece of Cornish granite will show that it is a mixture of at least four constituents—silvery flakes of mica; black patches of schorl; whitish crystals of felspar; and clear glassy crystals of quartz. A photograph of a thin slice of this rock, as it appears under the microscope magnified about 50 diameters, is

shown in Fig 2 Although the particles of felspar, mica, schorl, and quartz differ from one another in size and shape, no essential difference can be detected in the composition and properties of different samples of pure quartz, pure felspar, mica, and schörl Hence, it is inferred that the sample of granite is a mixture of schorl, felspar, quartz, and mica, and that each of these minerals is a true chemical compound. Very frequently, the constituents of a mixture are too small to be distinguished by simple inspection, and the body appears homogeneous. A microscopic examination may reveal the heterogeneous character of the substance Blood and milk, for instance, appear to be homogeneous fluids, but under the microscope the former appears as a colourless fluid with red corpuscles in suspension, and milk appears as a transparent liquid containing innumerable white globules (fat) Naturally, too, the stronger the magnification, the greater the probability of detecting whether the body is homogeneous or not Sometimes the microscope fails to detect non homogeneity under conditions where other tests indicate hetero geneity [1]

Before constant composition can be accepted as a proof of chemical combination, it must also be shown that the substance is homogeneous A homogeneous substance is one in which every part of the substance has exactly the same composition and properties as every other part. A substance may have a fixed and constant composition and yet not be homogeneous—*e.g*, cryohydrates and eutectic mixtures to be described later A substance may be homogeneous, for all we can tell to the contrary, and yet not have a constant composition—*e g* atmospheric air, a solution of sugar in water, etc This simply means that *all chemical compounds are homogeneous, but all homogeneous substances are not chemical compounds* Indeed, it is sometimes quite impossible to tell by any single test whether a given substance is a mixture or a true chemical compound

3 **The constituents of a mixture can usually be separated by mechanical processes**—The properties of a mixture of finely powdered iron and sulphur have been used in chemical text books since 1823 to illustrate the difference between mixtures and compounds. It would be difficult to find a better example Rub together a mixture containing, say, 6 grams of iron and 4 grams of sulphur in a mortar, and note that (1) the colour of the mixture is intermediate between the colour of the iron and of the sulphur, (2) the particles of iron and sulphur can be readily distinguished under the microscope, (3) some of the iron can be removed without difficulty by means of a magnet, and (4) the two can be separated quite readily by washing the mixture on a dry filter paper by means of carbon disulphide The sulphur dissolves in the carbon disulphide, the solution can be collected in a dish placed below the filter paper, and the sulphur can be recovered by allowing the carbon disulphide to evaporate from the dish Sulphur remains behind as a crystalline residue (Fig 148) The metallic iron remains on the filter paper Here then the constituents of the mixture have been separated by the mechanical processes—magneting, and the action of solvents. It is not always possible to apply

[1] See a later section on "Ultramicroscopic Particles" It may seem curious to refer a student to a later chapter The reference, of course, is intended when the book is read a second time, not the first time A text-book should be read forwards *and* backwards

these tests Solvents, as we shall find later, sometimes decompose a compound into its constituents, or conversely, "cause" the constituents of a mixture to combine

4 **A mixture usually possesses the common specific properties of its constituents, the properties of a compound are usually characteristic of itself alone**—The properties of a mixture are nearly always additive, *i e*, the resultant of the properties of the constituents of the mixture. For instance, a mixture of equal parts of a white and black powder will be grey. The specific gravity of a mixture of equal volumes of two substances of specific gravity[1] 3 and 5 will be 4, because if one c.c of water weighs one gram, there will be a mixture of 0 5 c c weighing 1 5 gram of one substance, 0 5 c c of the other substance weighing 2 5 grams, and 1 5 + 2 5 = 4 grams per c c It must be added that such properties of compounds are additive, for they are the sum of the properties of their constituents

EXAMPLES—(1) What is the specific gravity of air containing a mixture of one volume of oxygen and four volumes of nitrogen when the specific gravity of oxygen is 16, and the specific gravity of nitrogen, 14 01 ? One fifth volume of oxygen weighs 3 2 units, and four-fifths volume of nitrogen weighs 11 2 units Hence, one volume of the mixture will weigh 14 4 units when one volume of oxygen weighs 16 units

(2) Ozonized air—a mixture of air and ozone—has a specific gravity 1 3698, and it contains 13 84 per cent by weight of air, specific gravity unity and 86 16 per cent of ozone What is the specific gravity of ozone ? Here 13 84 grams of air occupy 13 84 ÷ 1 volumes, and 86 16 grams of ozone occupy 86 16 ÷ x volumes where x denotes the specific gravity of ozone Hence, 100 grams of ozonized air occupy 100 ÷ 1 3698 = 73 volumes Hence, 73 00 = 86 16 ÷ x + 13 84, or x = 1 456

If a portion of the mixture of sulphur and iron indicated above be placed in a hard glass test-tube, and warmed over the Bunsen's flame, the contents of the tube begin to glow and a kind of combustion spreads throughout the whole mass When cold, break the test-tube, and note that (1) the porous black mass formed during the action is quite different from the original mixture, (2) the microscope shows that the powdered mass is homogeneous, (3) it is not magnetic like iron,[2] and (4) it gives up no sulphur when digested with carbon disulphide[3] These facts lead to the assumption that there has been a chemical reaction between the sulphur and the iron. *When chemical combination occurs, the reacting constituents appear to lose their individuality or identity more or less completely, and each new substance which is formed has its own distinctive properties*

[1] SPECIFIC GRAVITY —The student is supposed to know that *specific gravity is a number which expresses how much heavier a given substance is than an equal volume of water taken at a standard temperature and pressure* In the case of gases either air = unity, oxygen = 16, hydrogen = 1, or hydrogen = 2 is taken as standard, and in the case of liquids and solids, water at +4°, or at 0°, is taken as unity. The great value of specific gravity data lies in the fact that *specific gravity is a number which enables volume measurements to be converted into weights, and weight measurements to be converted into volumes* Specific gravity may thus be regarded as the weight of unit volume if the standard water = 1 be taken, and the weights are reckoned in grams, and volumes in cubic centimetres There is no need here to distinguish between density and specific gravity

[2] This provided the iron was not in excess

[3] This provided the sulphur was not in excess, but the excess of sulphur if present can often be driven off as vapour

5 Thermal, actinic (light), or electrical phenomena usually occur during chemical changes —Attention must be directed to the fact that a great deal of heat was developed during the combination of the iron and sulphur The heat required to start the reaction does not account for the amount of heat developed during the reaction This point is perhaps better emphasized by placing an intimate mixture of powdered sulphur and zinc on a stone slab After the flame of a Bunsen's burner has been allowed to play on a portion of the mixture for a short time to start the reaction, the zinc and sulphur combine with almost explosive violence A large amount of heat and light are developed during the reaction

If a plate of commercial zinc be placed in dilute sulphuric acid, bubbles of gas are copiously evolved, and if a thermometer be placed in the vessel, the rise of temperature shows that heat is generated during the chemical action If the zinc be pure, very little if any gas is developed. It makes no difference if a plate of platinum be dipped in the same vessel as the zinc, provided the plates are not allowed to come into contact with one another If the two plates are connected by a piece of copper wire, a rapid stream of gas bubbles arises from the surface of the platinum plate, and some gas also comes from the zinc plate The platinum is not attacked by the acid in any way, but the zinc is rapidly dissolved. If a voltmeter be interposed in the circuit between the two plates—Fig 3—the deflection of the needle shows that an electric current "passes" from the platinum to the zinc, as represented by the arrows. The electric current is generated by the chemical reaction between the zinc and the acid, which results in the formation of zinc sulphate and a gas. The action will continue until all the acid or the zinc is used up.

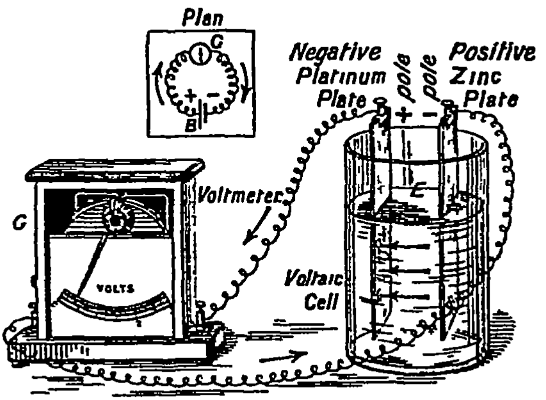

FIG 3 —Electricity by Chemical Action—Voltaic Cell

Nomenclature —The junction of the wire with the zinc plate is conventionally called the negative or − pole and the junction of wire with the platinum plate is called the positive or + pole For convenience, the zinc or positive plate of the cell *B* is often represented by a short thick line, and the platinum or negative plate by a longer thinner line as illustrated by the plan Fig 3 Hence the platinum in this simple cell is called the positive pole, or negative plate, and the zinc is the negative pole or positive plate Here *G* represents the voltmeter or galvanometer The vessel of acid with its two plates is called a voltaic cell, and this particular combination can be symbolized —

Platinum | Dilute sulphuric acid | Zinc

The chemical reaction just indicated is far from being the most economical mode of generating electricity, but all the different forms of voltaic cell on the market agree in this Electricity is generated during chemical action

The development of heat, light, or electrification are common concomitants of chemical action. The absence of such phenomena when substances are simply mixed together is usually taken as one sign that chemical action has not taken place. When nitrogen and oxygen are mixed together in suitable proportions to make atmospheric air, there is no sign of chemical action, and this fact is sometimes cited among the proofs that air is a mixture

Summary —The tests for distinguishing chemical compounds from mixtures involve answers to the following questions

1 Are the different constituents united in definite and constant proportions ?
2 Is the substance homogeneous ?
3 Are the properties of the substance additive ?
4 Were thermal actinic or electrical phenomena developed when the substance was compounded ?
5 Can the constituents be separated by mechanical processes ?

Mechanical processes of separation —The so called mechanical processes of separation usually include. (1) Magneting, hand-picking, sieving, elutriation, etc , (2) If some mixtures be placed in liquids of the right specific gravity, the lighter constituents will float, and the heavier constituents will sink; (3) Differences in the solubility of the constituents in suitable solvents, (4) Distillation, freezing, etc

It may be useful to again emphasize the fact that the so called "mechanical" processes of separation, involving solution, freezing, and distillation, are not always satisfactory tests for distinguishing chemical compounds from mechanical mixtures It is generally stated that "a solution of sugar or of salt in water is a mechanical mixture because, though homogeneous, the salt or sugar can be recovered unchanged from the water by the mechanical process of evaporation " This is an unwarranted assumption The salt and water may have combined, and the product of the chemical combination may be decomposed into salt and water during the process of evaporation

The above list does not exhaust the available tests, but in spite of what we know, there is sometimes a lingering doubt whether a particular substance is a mixture or a true chemical compound This arises from the fact that some of the tests are impracticable, others are indecisive As previously stated, owing to our ignorance, it is not always easy to state "the truth and nothing but the truth"

§ 4. Circumstantial and Cumulative Evidence

To find the truth is a matter of luck, the full value of which is only realized when we can prove that what we have found is true Unfortunately, the certainty of our knowledge is at so low a level that all we can do is to follow along the lines of greatest probability —J J BERZELIUS

Suppose a substance is suspected to be a chemical compound because it appears to be homogeneous , on investigation, we find that it has a fixed definite composition This verifies our first suspicion, and the joint testimony gives a very much more probable conclusion than either alone By piling up the evidence in this manner, for or against our suspicion, we can make a chain of circumstantial evidence which enables highly probable conclusions to be drawn Each bit of evidence taken by itself is not of much value, but all the evidence taken collectively has tremendous

weight It is easy to see, too, that the probability that an hypothesis is valid becomes less as the number of unproved assumptions on which it is based becomes greater

We can even get a numerical illustration *If* the definite compound test be right nine times out of ten, the probability that a given substance of definite composition is not a true compound is $\frac{1}{10}$, similarly, *if* the homogeneous test be right three times out of four, the probability that the given homogeneous substance is not a chemical compound is $\frac{1}{4}$, and the probability that the given homogeneous substance of definite composition is not a true compound is $\frac{1}{40}$ Every bit of additional evidence in favour of a conclusion multiplies the probability of its being correct in an emphatic manner, and evidence against a conclusion acts similarly in the converse way Huxley has stated that one of the tragedies in science is the slaughter of a beautiful hypothesis by one *incongruent fact*, a conclusion based solely upon circumstantial evidence is always in danger of this Damoclean sword

A writer has said "When two facts seem to be in conflict, we may be driven to decide which is the more credible of the two" This statement may give rise to a misunderstanding We cannot admit the possibility of two contradictory facts. Facts can, and often do, contradict hypotheses. Again, a fact is a fact and cannot be disputed If there be any doubt about the truth of an alleged fact something is wrong The laboratory, not the study, is the place to decide if the alleged fact is the result of an incomplete or of a mal observation Facts *quâ* facts cannot be graded in degrees of probability or credibility

§ 5 Analysis and Synthesis

> It is surely not fitting for a chemist to make a large number of experiments with the sole object of rapidly making new products, for he will then over look phenomena and changes during the operations which might serve as important clues to an explanation of nature's secrets —M W LOMONOSSOFF

The term *synthesis*—from the Greek σύν (syn), with, τιθέω (titheo), I place—is employed for the operations involved in making a particular compound from its constituents *E g*, methods for the synthesis of ferrous sulphide, and also for the synthesis of various oxides, were described in preceding sections The term *analysis*—from the Greek ἀνά (ana), back, λύω (lyo), I loosen—is employed for the process of separating the constituents of a compound or mixture Thus mercuric oxide is broken down into its constituents when heated The object of the analysis may be to answer the question What are the constituents of the mixture or compound? The analysis is then said to be *qualitative* If the relative quantities of the different constituents are to be determined, the analysis is said to be *quantitative*. For instance, if a weighed portion of a mixture of sulphur and iron be treated with carbon disulphide as described above, and the separated sulphur and iron be weighed, the two weights should be nearly equal to the weight of the original mixture taken for the analysis. The numbers so obtained express the result of a quantitative analysis of the mixture

Analysis of gunpowder —Gunpowder is a mixture of nitre (soluble in water), sulphur (soluble in carbon disulphide), and carbon (insoluble in both the solvents just mentioned) Hence, gunpowder can be analysed

by first washing a weighed quantity of the powder on a filter paper with warm water, and collecting and evaporating the filtered solution to dryness in a weighed dish. The increase in the weight of the dish with its contents represents the amount of nitre. The insoluble residue is dried and treated in a similar manner with carbon disulphide, and the amount of sulphur determined as in the case of the mixture of iron and sulphur. The dried carbon is then weighed. The result of a quantitative analysis of a sample of gunpowder, expressed in percentage numbers, is: nitre, 78 per cent.; sulphur, 12 per cent.; charcoal, 10 per cent. For the appearance of the residual nitre (potassium nitrate) left on evaporating the aqueous solution, see Fig. 178 (left), and for the sulphur residue, Fig. 148.

There was one period in the history of chemistry when the discovery or synthesis of new substances was considered to be the main aim of the chemist, and the style of some old text-books on chemistry was not far removed from that of cookery-recipe books. This work has been useful, for it has furnished modern chemistry with raw empirical material to be worked up into science. Modern chemistry therefore is not so much directed to the discovery of new compounds, as to a more careful study of the old. We are beginning to recognize the truth of the inspired words of M. W. Lomonossoff, cited above, though written in 1751, and the growing use of "squared paper" in chemical text-books is "a sign of the times."

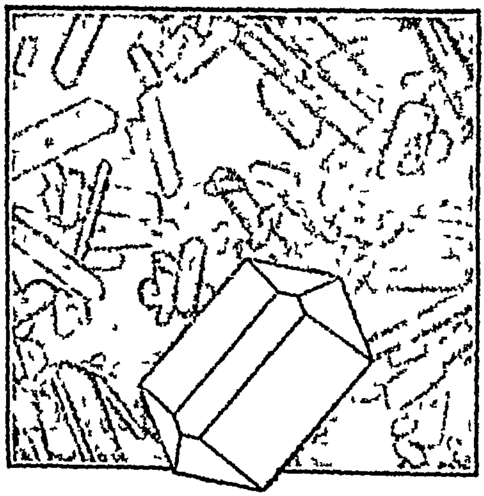

FIG. 4.—Crystals of Zinc Sulphate (× 50).

Synthesis of zinc sulphate.—The solution which remains when the dilute sulphuric acid, indicated on p. 20, can dissolve no more zinc, may be filtered and evaporated over a hot plate until a drop of the hot solution crystallizes when placed on a cold glass plate. Crystals of zinc sulphate will separate as the solution cools. By evaporating a large volume of the solution very slowly, crystals over a foot long have been obtained. The appearance of the crystals which separate from a drop of solution slowly evaporated is indicated in Fig. 4, and an outline drawing of a perfect crystal is shown on the same diagram. This experiment illustrates the synthesis of zinc sulphate from metallic zinc and dilute sulphuric acid.

The analysis of aqueous solutions of zinc sulphate by the electric current.—In the experiment illustrated by Fig. 3, an electric current was developed during the reaction between dilute sulphuric acid and metallic zinc which resulted in the formation of zinc sulphate. Fit up a similar arrangement as before, but place two platinum plates, *E*, and pure distilled water in the clean glass jar, which will now be called the "electrolytic cell." Connect the two platinum plates with an accumulator or secondary battery, and a voltmeter as indicated in Fig. 5. The object of the

accumulator is to generate an electric current.[1] If the water is pure, the needle of the voltmeter moves very little, if at all. Add a concentrated solution of zinc sulphate to the water in the glass jar The jump of the needle of the voltmeter shows that a current of electricity is flowing through the circuit, and hence also through the solution of zinc sulphate If chloroform, benzene, or an aqueous solution of cane sugar had been used in place of the solution of zinc sulphate in the electrolytic cell, no current would pass through the circuit. Hence liquids may be either conductors or non conductors of electricity The current which passes through the solution of zinc sulphate produces some remarkable changes (1) a spongy mass of metallic zinc accumulates about one of the platinum plates, (2) if the solution be tested, particularly in the neighbourhood of the other platinum plate, sulphuric acid will be found to be accumulating in the solution during the process of electrolysis and (3) bubbles of oxygen gas, easily tested by collecting some in a test-tube, rise from the same platinum plate

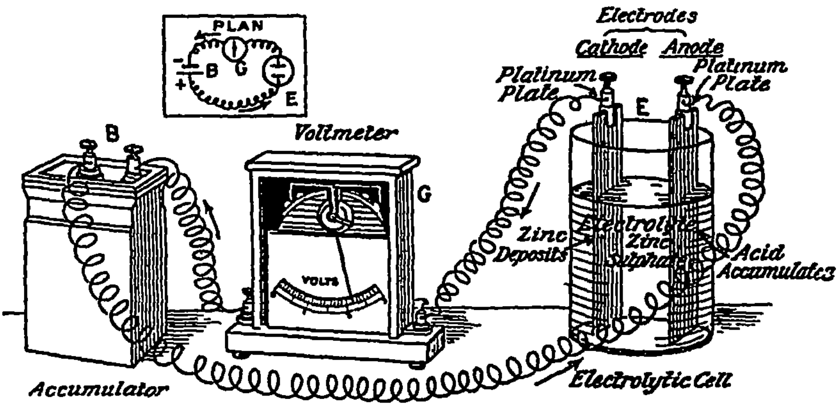

FIG 5 —Chemical Action induced by Electric Current—Electrolysis

about which the acid accumulates If the experiment be continued long enough, and the products of the action be examined, we shall find that metallic zinc and sulphuric acid have been produced If the accumulator be disconnected, and the connections be made as indicated in Fig 3, the zinc will redissolve in the acid, re producing zinc sulphate, and an electric current will be generated during the dissolution of the zinc

Nomenclature —The process of decomposition or analysis by the aid of the electric current is called **electrolysis** The liquid which is decomposed is called the **electrolyte** The passing of the electric current through the conducting copper wires, and through the conducting platinum plates, produces no change in these metals Hence, we recognize two kinds of conductivity—in one the conducting medium is decomposed by the current—electrolyte, and in the other the conducting medium is not decomposed by the current—non electrolyte The plate at which the zinc collects is called the **cathode**—from the Greek κατα (kata) down ὁδός (odos) a path—and the other plate about which the acid collects, is called the **anode**—from the Greek ἀνα (ana) up, ὁδός (odos), a path The anode and cathode together are called the **electrodes** With the conventions indicated on p 20 as to the direction of the electric current, the current is said to enter the electrolytic cell *via* the anode, and to leave the cell *viâ* the cathode The two

[1] This is a better way of using electricity than working with a primary battery Fig 3

electrodes are thus "the doors or ways by which the current passes into or out of the decomposing body" It seems as if the electric current first splits the decomposing liquid into two parts which pass to the electrodes The term anions—from the Greek ἰών (ion), traveller—is applied to those parts of the decomposing fluid which go to the anode; and those passing to the cathode are called cations, and when reference is made to both the anions and cations the term ions is employed "Ions" is thus a general term for those bodies which pass to the electrodes during electrolysis This notation was proposed by M Faraday in 1834 The subject will be further developed in later chapters.

The principle of reversibility—The experiments indicated above illustrate an important principle—the principle of reversibility If an antecedent event A produces an effect B, then an antecedent event B will reduce the effect A Thus, chemical action can produce an electric current, Fig 3, and conversely an electric current results in a loss of chemical activity (in the battery), Fig 5 The one can undo the work of the other Other examples of the principle will be found as we progress in our studies Heat causes gases to expand, conversely, if a gas expands by its own elastic force, heat will be lost and the gas cooled, etc

§ 6 Pure Substances

> Pure water is never found in nature One may even say that no man has ever seen or handled absolutely pure water It is an ideal substance, to which some specimens of highly purified water have nearly approached —M M P Muir

The substance we call water has its own specific properties, but sea water, spring-water, rain-water, and distilled water show certain differences in their properties The differences, however, are not due to the water, but to the substances—impurities—which the water has dissolved from its surroundings. If sea water be distilled, the "impurities"—sodium chloride, magnesium chloride, etc—remain behind. Sea water is therefore a homogeneous substance, but, rightly or wrongly, it is often stated to be a mixture, because water can be separated by simple evaporation or by freezing Table salt is more or less impure sodium chloride The presence of a little magnesium chloride in table salt makes the salt more hygroscopic, so that the contaminated table salt deliquesces[1] more readily than if magnesium chloride were absent

Lavoisier's experiments on the transformation of water into earth—A compound may be contaminated with impurities in many ways—from the raw materials used in preparing the compound; from the vessels in which it was prepared or stored, by exposure to the atmosphere, by the partial decomposition of the substance when exposed to light, etc It was once believed that air can be condensed to water, as was thought to be proved by "falling dew," and that water can be changed into an earth, as is evidenced by the residue obtained when rain water or distilled water is evaporated to dryness in glass vessels Lavoisier read a paper in 1770 with the idea of "settling by decisive experiments whether water can be changed into earth as was thought by the old philosophers, and

[1] The term *deliquescence* refers to the process of absorbing moisture from the air so that a salt becomes moist, or even dissolves in the moisture it has absorbed from the air *E g* expose potassium carbonate to the atmosphere by placing some crystals in a small dish and note the result The term *efflorescence* refers to the formation of a crust—generally white—on the surface of a body The phenomenon is—very often—due to the loss of water from certain crystalline salts *E g* expose crystals of washing soda to a dry atmosphere

still is thought by some chemists of the day" By distilling water in hermetically sealed glass vessels, weighed before and after the experiment, it can be proved (1) The earth does not come from outside the vessel, because the weight of the vessel *and* its contents does not alter, (2) The earth does not come from the water, because the weight of the water remains the same before and after the experiment, (3) The earth comes from the vessel, because the vessel loses in weight, and (4) The earth comes *wholly* from the vessel, because the loss in weight of the vessel is virtually equal to the weight of the earth formed Hence, adds Lavoisier, "it follows from these experiments that the greater part, possibly the whole of the earth separated from rain-water by evaporation, is due to the solution of the vessels in which the water has been collected and evaporated"

The purity of commercial compounds—The term "*pure,*" or "*chemically pure,*" is unfortunately used when it is desired to emphasize the fact that a substance is not contaminated with sufficient impurity to appreciably influence the most exact work for which the substance is to be employed There cannot be degrees of "purity" A thing is either "pure" or "impure" It may be convenient to use terms like "highly pure," "all but pure," "very impure," etc, but the term "chemically pure" in the sense of "nearly pure" is objectionable "Chemically pure" substances, paradoxical as it may seem, are sold with a statement on the labels indicating what impurities are present as well as how much of each A *commercial* reagent, on the other hand, has not been specially purified and hence is sold at a cheaper rate than the "chemically pure" chemicals Purification is an expensive operation, and the cheaper commercial reagents[1] are used whenever specially purified materials are not required Some hold that "perfectly pure substances are unknown" This is probable, but to establish the proposition, we should be involved in a metaphysical discussion, and we might be led to say with A. Laurent "Chemistry is the science of substances which do not exist"

The effect of traces of impurity on the properties of a compound.—It may be well to emphasize, just here, that sometimes a minute trace of impurity is of vital importance Some reactions proceed quite differently in the presence, and in the absence of traces of impurity The properties of many substances, too, are modified in a remarkable manner by small traces of impurity H Vivian says that $\frac{1}{1000}$ part of antimony will convert the best selected copper into "the worst conceivable", Lord Kelvin says that the presence of $\frac{1}{1000}$ part of bismuth in copper would reduce its electrical conductivity so as to be fatal to the success of the submarine cable, and W R Roberts Austin says that $\frac{1}{500}$ part of bismuth in gold would render gold useless, from the point of view of coinage, because the metal would crumble under pressure in the die

§ 7 Dalton's Law of Multiple Proportions

If Dalton's hypothesis of multiple proportions be found correct, we shall have to regard it as the greatest advance chemistry has yet made towards its development into a science —J J BERZELIUS, 1811

The formation of chemical compounds is not a capricious and fortuitous process, but it proceeds in an orderly fashion Chemical combination is

[1] The terms *reagents* and *chemicals* are applied to the substances used in chemistry for producing special reactions with other substances The term "re agent" is more particularly used in analytical work.

restricted to certain fixed proportions of matter These limitations appear to have been prescribed by nature as part of her scheme in building the material universe This fact arrested the attention of J Rey in 1630. Rey's conclusion that in the calcination of the metals "nature has set limits which she does not overstep," agrees with many facts, but there are certain limitations If one gram of lead be calcined for a long time at 500°, never more than 1 103 gram of a red powder—red lead—is obtained. Here, 64 grams of oxygen correspond with 621 grams of lead If the lead be calcined at about 750°, one gram of lead will not take up more than 0·078 gram of oxygen to form a yellow powder—litharge, otherwise expressed. 64 grams of oxygen correspond with 828 grams of lead Here then nature has set *two* limits, lead forms at least two definite oxides—a red oxide stable at a dull red heat, and a yellow oxide stable at a bright red heat. The relative proportions of lead and oxygen in the two oxides are as follows

	Oxygen	Lead
Red oxide (red lead)	64	621 = 207 × 3
Yellow oxide (litharge)	64	828 = 207 × 4

This means that for a given weight of oxygen, the yellow oxide has four-thirds as much lead as the red oxide Similarly, carbon forms two well defined oxides called respectively carbon monoxide, and carbon dioxide In these we have

	Oxygen	Carbon.
Carbon dioxide	8	3 = 1 × 3
Carbon monoxide	8	6 = 2 × 3

At least six oxides of nitrogen are known In these, the relative proportions of nitrogen and oxygen are as follows.

	Nitrogen	Oxygen
Nitrogen monoxide	14	8 = 1 × 8
Nitrogen dioxide	14	16 = 2 × 8
Nitrogen trioxide	14	24 = 3 × 8
Nitrogen tetroxide	14	32 = 4 × 8
Nitrogen pentoxide	14	40 = 5 × 8
Nitrogen hexoxide	14	48 = 6 × 8

These six compounds of the same elements united in different proportions form a series of substances so well marked and contra-distinguished that it is questionable if the most acute human intellect would ever have guessed that they contained the same constituents Starting from the compound with the least oxygen, we see that for every 14 grams of nitrogen, the amount of oxygen increases by steps of 8 grams Accordingly, in all six compounds of nitrogen and oxygen, the masses of nitrogen and oxygen are to one another as $m \times 14 : n \times 8$, where m and n are whole numbers Hundreds of cases equally simple might be cited Similar facts led J Dalton (1802–4) to the generalization now called the law of multiple proportions when one substance unites with another in more than one proportion, these different proportions bear a simple ratio to one another

There is no difficulty in tracing the "simple ratio" $m : n$ in the cases which precede, but it is not always easy to detect the *simplicity* of this ratio in perhaps the larger number of cases. For instance, the ratio $m : n$ for compounds of carbon and hydrogen passes from 1 : 4 in methane, up to 60 : 122 in dimyricyl, and still more complex cases are

not uncommon Still, the law is considered to be so well founded that it can be applied to predict the composition of compounds which have never been prepared. Thus, if an oxide of nitrogen containing rather more oxygen than nitrogen hexoxide be made, we may predict that it will contain 7 × 8 = 56 parts of oxygen for every 14 parts of nitrogen by weight. Again, if a substance be found to contain oxygen and nitrogen, not in the proportion 14 8 or a multiple of 8, it is in all probability a mixture, not a true compound. Thus, air contains oxygen and nitrogen, but the proportions of nitrogen to oxygen is as 14 4 29 This is usually given along with other circumstantial evidence to show the probability that air is a mixture and not a chemical compound

We might easily be led to reason in a vicious circle (*in circulo probando*) by a rigid application of the so called multiple proportion law A salt dissolves in water in all proportions up to a certain limiting value. The process of solution, in some cases, seems to be otherwise indistinguishable from chemical combination It is sometimes said that the process of solution cannot be a case of chemical combination because there are no signs of abrupt *per saltum* changes characteristic of combination in multiple proportions More bluntly expressed a prejudice in favour of the generalization in question may warp the judgment to such an extent as to lead to a denial of the possibility of contradictory phenomena Such a perversion of the judgment must be detrimental to the progress of science Hence the danger of cherishing a blind faith in our so called "laws of nature" (*Cf* p 473)

§ 8 Richter's Law of Reciprocal Proportions

> After long and painful centuries of continuous effort, chemistry has discovered that the elements combine with one another in definite and unchanging ratios of quantity, and that, when their compounds are decomposed, they yield up those identical ratios —S BROWN (1843)

Between 1810 to 1812, J J Berzelius published the results of a careful study of the quantitative relations of some of the elements He found that 100 parts of iron, 230 parts of copper, and 381 parts of lead are equivalent, for they unite with 29 6 parts of oxygen forming oxides, and with 58 73 parts of sulphur, forming sulphides. Hence, since 58 73 parts of sulphur and 29 6 parts of oxygen unite respectively with 381 parts of lead, then, if sulphur and oxygen unite chemically, 58 73 parts of sulphur will unite with 29 6 parts of oxygen, or, taking the law of multiple proportions into consideration, with some simple multiple or submultiple of 29 6 parts of oxygen In confirmation, Berzelius found that in sulphur dioxide, 58 73 parts of sulphur are united with 57 45 parts of oxygen The difference between 2 × 29 6 = 59 2 and 57 45 is rather great, but some of the methods of analysis were crude in the time of Berzelius, and very much closer approximations—very nearly 1 in 50,000—have been obtained in recent years

J B Richter, some twenty years before Berzelius' work, proved that a similar relation held good for the combination of acids and alkalies. Berzelius extended Richter's law[1] to combinations between the elements The above relations are included in the generalization sometimes

[1] C F Wenzel 1777, is sometimes said to be the father of this generalization This, however, appears to be an historical error

called the law of reciprocal proportions, or the law of equivalent weights The weights—multiple or submultiple—of the various elements which react with a certain fixed weight of some other element, taken arbitrarily as a standard, also react with one another. If two substances, A and B, each combines with a third substance C, then A and B can combine with each other only in those proportions in which they combine with C or in some simple multiple of those proportions The laws of constant, multiple, and reciprocal proportions are wonderful examples of the beauty and harmony of nature, and yet we have hints that these are but symbols of a sublimer generalization which, when discovered,

> Will make one music as before
> But vaster

If a compound be formed by the union of two elements A and B, it is only necessary to find the proportion in which a third element C unites with one of the two elements say A, to determine the proportions in which C unites with B These numerical relations come out very clearly by comparing the proportions in which the different members of a series of elements, selected at random combine with a constant weight of several other elements Suppose the analysis of a substance shows that its ingredients are not in those proportions which we should expect from the known combinations of each of its components with another substance, we might safely infer that the substance analyzed is a mixture, and not a single compound

§ 9 Combining, Reacting, or Equivalent Weights.

> Since it is already settled for us by custom that quantities of different substances are to be called equal when or because they are equivalent gravimetrically, we have no choice but also, from the chemical point of view, to call those quantities of substance equal which interact in single chemical changes —F Divers, 1902

The following numbers represent the results obtained by the chemical analysis of a number of substances selected at random

		Per cent		Per cent
Silicon dioxide	Silicon	46 93,	Oxygen	53·07
Hydrogen chloride	Hydrogen	2 76,	Chlorine	97 23
Magnesium chloride	Magnesium	25 53,	Chlorine	74 47
Water	Hydrogen	11 18	Oxygen	88 81
Silver chloride	Silver	75 26,	Chlorine	24 74
Silver fluoride	Silver	70 05,	Fluorine	29 95

Analyses are generally calculated so that the sum of the constituents, all together, is 100 (per cent) within the limits of experimental error This is simply a convention of the analyst, for the results could be just as intelligibly summed to any other number Taking any one of the elements as a standard, let us calculate what amount of each of the other elements will combine with a given quantity of the selected element To save time, take oxygen = 8 as the standard Starting with silicon, 53 07 parts of oxygen are combined with 46 93 parts of silicon Consequently, we have the proportion

$$53\ 07 : 8 = 46\ 93 : x, \text{ or, } x = 7\ 07$$

for silicon when oxygen = 8 Similarly, for water, hydrogen is 1 008 when oxygen is 8 Again, in hydrogen chloride when hydrogen is 1·008, chlorine is 35 45, in silver chloride, silver is 107 88 when chlorine is 35 45,

when silver is 107 88, fluorine is 19, and when chlorine is 35 45, magnesium is 12 16 Collecting together the results of these calculations, we get

Oxygen	Silicon	Hydrogen	Chlorine	Silver	Fluorine	Magnesium
8	7 07	1 008	34 45	107 88	19	12 16

We have previously obtained a number of results for some metals for the standard O = 8 by a different process, and the number for magnesium obtained by an indirect process Oxygen → hydrogen (water) → chlorine (hydrogen chloride) → magnesium (magnesium chloride) gives the same result within the limits of experimental error as was obtained by a totally different process Similar results are obtained in all cases, subject, of course, to the greater risk of experimental error when a long chain of compounds is involved As a rule, there is no need to follow such an extended series as we have done here for fluorine and magnesium Most of the elements unite directly with oxygen, and with the other elements, one intermediate step usually suffices.

We are therefore able to deduce these important generalizations **A number can be assigned to each element, this number—called the combining, reacting, or equivalent weight—represents the number of parts by weight of the given element which can enter into combination with 8 parts by weight of oxygen, or one part by weight of hydrogen.** All combining weights are relative numbers, and they are conventionally referred to oxygen = 8, or hydrogen = 1 When an element unites with another element in more than one proportion, the higher proportions will always be simple multiples of the combining weights—one for each element **This is the so called law of combining or reacting weights when substances enter into chemical combination they always do so in quantities proportional to their combining weights**

If the combining weights of the elements are fixed, as they undoubtedly are, and since the elements can combine to form compounds which, in turn, can form compounds with other elements and with one another, it follows that the compounds themselves also have combining weights if they also can enter into chemical combination. Hence the so called law of **compound proportion—the combining weight of a compound body is the sum of the combining weights of its components** This deduction from the law of combining weights is as firmly established experimentally as the law of combining weights itself The neutralization of acids by bases, and numerous chemical reactions, can be cited in illustration

The experimental results stated on p 8, Table I., raise the suspicion that *there is a difference between chemical and gravimetric equality* In the latter, equal quantities of the different forms of matter are represented by equal weights, whereas, in a chemical sense, equal quantities of matter are the weights or masses of different forms of matter which unite with one another chemically Consequently, chemical union may be regarded as a measure of the amounts of the different forms of matter which are chemically equivalent Chemical equality is thus as clearly defined as gravimetric equality The former is a measure of chemical and the latter a measure of physical phenomena, the latter is wholly independent of, and the former mainly dependent upon the nature of the substances compared

§ 10 The Law of the Conservation or Persistence of Weight.

The annihilation of matter is unthinkable for the same reason that the creation of matter is unthinkable, the reason namely that nothing cannot be an object of thought —H SPENCER.

It will be remembered that Lavoisier (1774) heated tin with air in a closed vessel and found that the weight of the whole system, before and after the calcination of the tin, was the same, thus showing that the whole system had neither gained nor lost in weight This experiment is mentioned because it emphasizes, very well, the fact that in spite of the most painstaking care, every time all the substances taking part in a chemical reaction are weighed before and after the change, there is no sign of any alteration in the quantity of matter This fact is sometimes called the law of the indestructibility of matter As Democritus has said nothing can never become something, nor can something become nothing—*ex nihilo nihil fit, et in nihilum nihil potest reverti* The principle of the indestructibility of matter was tacitly assumed by many old investigators A L Lavoisier is generally supposed to have first demonstrated the law in 1774 by experiments like that cited above, but the law was definitely enunciated in 1756 by M W Lomonossoff, and the law must have been at the back of J Black's mind when he worked on the alkaline earths (*q v*) in 1755

The chemist's law of "the indestructibility of matter" really means that the total *weight* of the elements in any reacting system remains constant through all the physical and chemical changes it is made to undergo The observed facts are better generalized as the law of persistence of weight. no change in the total weight of all the substances taking part in any chemical process has ever been observed If A and B represent respectively the weights of two elements which take part in a chemical reaction producing the weights M and N of two other substances, the law of persistence of weights states that

$$A + B = M + N$$

If the weight of one of these four substances be unknown, it can be computed by solving the equation Chemists constantly use this principle in their work

When faith in magic was more prevalent than it is to day, many believed that by some (potent incantation) or charm, matter could be called out of nothingness, or could be made non existent [1] Superficial observation might lead to the belief that a growing tree, the evaporation of water, and the burning of a candle prove the creation and the destruction of matter, but a careful study of these and innumerable other phenomena, has shown that the apparent destruction of matter is an illusion Matter may change its state as when liquid water is vaporized, and when a candle is burnt In the case of a growing tree, the nutrition the tree receives from the soil and from the air (carbon dioxide) is overlooked Fig 6 illustrates an instructive experiment which is commonly used to show that the apparent destruction of matter in the burning of a candle is illusory A candle, *A*, is fixed on one pan of a balance below a cylinder *B* A piece of coarse wire gauze, *C*, is fixed in the lower part of the cylinder *B* The

[1] H Spencer considers that all the so-called experimental proofs by weighing tacitly assume the object being proved, since weighing implies that the matter forming the weights remains relatively unchanged in quantity.

wire gauze supports a few lumps of quicklime[1] on which rests a mixture of *granulated soda lime and glass wool*—the latter to prevent the soda lime clogging the tube. Weights are added to the right scale pan until the beam of the balance is horizontal. The candle is lighted. The gases rising from the flame pass through the cylinder *B*—and the products of combustion are absorbed by the soda lime. In 3 or 4 minutes the pan carrying the candle is depressed as illustrated in the diagram. The increase in weight is due to the fixation of the products of combustion by the soda lime. The products of combustion are formed by the com-

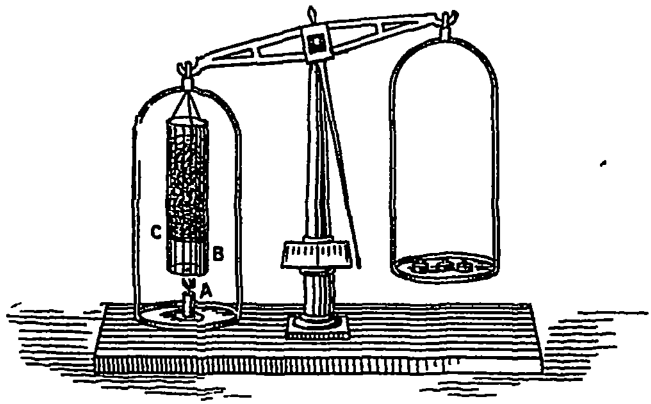

FIG 6.—Apparent Increase in Weight during Combustion (after H. E. Roscoe and C. Schorlemmer)

bination of the carbon and hydrogen of the candle with the oxygen of the air. The oxygen of the air was not weighed in the first weighing.

Every time a chemical reaction takes place in a closed vessel, which permits neither the egress nor the ingress of matter, the total weight remains unchanged within the limits of experimental error. The more carefully the experiments are made, the more nearly do the values approach identity. Both A. Heydweiller (1901) and H. Landolt (1893) have tried to find if a loss in weight occurs during chemical action. Their experiments may be illustrated by introducing a solution of silver nitrate into one limb of the λ shaped tube *B*, Fig 7, by means of the funnel *A*, and a solution of potassium chromate in the other limb. The tube is then weighed and tilted so as to mix the solutions and start the reaction. There is no difference in the weight of the tube, before and after the reaction, within the limits of the experimental error ± 0.000030 grm. In Landolt's experiments the opening of the tube *B* was sealed up before the solutions were mixed. Other pairs of solutions are: a solution of potassium iodate slightly acidulated with hydrochloric acid and potassium iodide; lead acetate and sodium sulphide; acidulated potassium chromate and sodium sulphite, etc. After an examination of fifteen different reactions, Landolt (1909) failed to detect a variation in weight, and "since there seems no

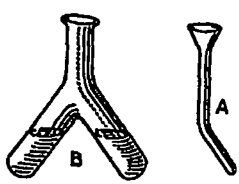

FIG 7.—Landolt's Tube

[1] To prevent water dripping on to the flame.

prospect of pushing the precision of the experiments further than the degree of exactness attained, the experimental proof of the law may be regarded as established" The law of the persistence of weight can thus be stated: **A variation in the total weight of the substances taking part in chemical reactions, greater than the limits of experimental error, has never been detected.**

It is quite conceivable that the weight of the iron in, say, magnetic oxide of iron might *appear* to weigh more than the same amount of iron in say, potassium ferrocyanide because of the effect of the earth's magnetic field upon the former But if such an effect were observed, it would not interfere with our faith in the law as soon as the disturbing effect was recognized.

§ 11 The Atomic Theory.

> It seems probable to me, that God in the beginning formed matter in solid, massy, hard, impenetrable, movable particles, of such sizes and figures, and with such other properties, and in such proportion to space, as most conduced to the end for which He formed them, and that these primitive particles, being solids, are incomparably harder than any porous body compounded of them, even so very hard as never to wear or break in pieces, no ordinary power being able to divide what God Himself made one in the first creation The changes of corporeal things are to be placed only in the various separations and new associations and motions of these permanent particles These principles I consider not as occult qualities, but as general laws of nature by which the things themselves are formed, their truth appearing to us by phenomena, though their causes be not yet discovered —ISAAC NEWTON

The four laws of chemical combination (1) the persistence of weight, (2) the law of constant composition, (3) the law of multiple proportions; and (4) the law of reciprocal proportions, summarize observed facts They exist quite independently of any hypothesis we might devise about the inner meaning of the facts, but we have an intuitive feeling that there must be some peculiarity in the constitution of matter which will account for the facts

An atom is the unit of chemical exchange.—Chemists in imagination have invested matter with a granular structure Matter is supposed to be discrete, and built up of corporeal atoms. The imagination can subdivide matter indefinitely, the chemist says that however true this may be, nothing less than an atom ever takes part in a chemical reaction The atom is the limiting size so far as chemical combination is concerned. An atom cannot be subdivided by any known chemical process What A Kekule wrote in 1867 applies equally well to-day, in spite of some interesting though abortive attempts to eliminate atoms from chemistry. Should the progress of chemistry lead to a different view of the constitution of matter, it will make little alteration to the chemist's atom The chemical atom will always remain the *chemist's unit* "As a chemist," wrote Kekule, "I believe that the assumption of atoms is not only advisable but absolutely necessary provided that the term be understood to denote those particles of matter which undergo no further division in chemical transformations"

Compare this hypothesis with observation Fix the attention on the facts Elements combine with one another either in amounts which correspond with their combining weights (law of constant composition), or with multiples of their combining weights (law of multiple proportions)

Otherwise expressed, definite amounts of matter—the atoms—corresponding with the combining weights act as chemical units Reactions between different elements are reactions between these units. Atoms of the same element all have the same constant weight,[1] and atoms of different elements have different combining weights All this is in agreement with the law of constant combining weights

Fractions of an atom do not take part in chemical changes—The proportions in which one element combines with another can alter only by steps one atom at a time 1, 2, 3, atoms of one element can combine with 1, 2, 3, *atoms of another element* This is but one way of stating the laws of multiple and reciprocal proportions. The weight of an atom of each element is a constant quantity, and therefore elements can only combine with each other in certain constant proportions or in multiples thereof The atoms of the elements are the units from which nature has fashioned all the different varieties of matter in the universe One atom of mercury unites with one atom of oxygen to form mercuric oxide. If two atoms of mercury united with one atom of oxygen, the result would not be mercuric oxide, but some other oxide of mercury—if otherwise, the law of constant composition would be false As a matter of fact, such a compound is known, but it is mercurous oxide. Mercurous oxide has its own specific properties which are different from those of mercuric oxide We thus adopt the view of J B Dumas and of M Faraday that "whether *matter* be *atomic* or *not*, this much is certain, granting it be atomic, it would behave in chemical transformations as it does now"

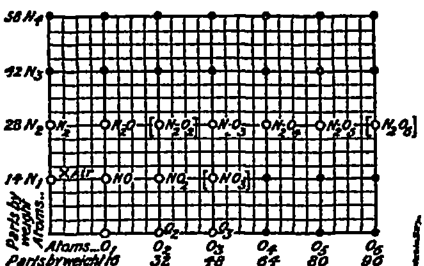

FIG 8.—Law of Multiple Proportions

The law of multiple proportions—The idea embodied in this law can be neatly illustrated by means of squared paper Let the abscissæ, Fig 8, represent weights of oxygen, and the ordinates weights of nitrogen which enter into combination with the oxygen If, for convenience, we take oxygen = 16, and nitrogen = 14 as standard weights for the respective atoms, the known unary and binary compounds of these elements appear at the points of intersection of lines representing 14, 28, 42 parts by weight of nitrogen, and 16, 32, 48 parts by weight of oxygen Let the symbol N represent one atom of nitrogen, N_2, two atoms of nitrogen, etc, and let O represent one atom of oxygen, O_2, two atoms of oxygen, etc Then the symbol N_2O, NO, etc, may be used to represent compounds containing the indicated number of atoms of each element The known compounds of these two elements are represented by symbols "o" in the diagram If the law of multiple proportions perfectly describes nature's *modus operandi*, and no other disturbing influence be at work, we can represent possible,[2] but yet undiscovered, compounds of nitrogen

[1] It might here be added that W Crookes (1887) found it expedient to assume as a working speculation that the atoms of the element yttrium "differ probably in weight, and certainly in the internal motions they undergo" There is, however, no direct proof of this because the law of constant proportions has always been found to hold rigorously within the limits of experimental error

[2] The symbols in brackets in the diagram represent compounds which we are

and oxygen by points "•", and compounds representable by the intermediate positions in the diagram are impossible Hence air, whose composition is represented by the cross "×" in the diagram, is not a chemical compound

Atomic weights are relative —We can express the combining weights of the atoms in terms of any unit we please, it is quite immaterial whether a gram or a ton be imagined In dealing with combining or atomic weights, the conception of absolute quantity is quite irrelevant. Given sufficient oxygen, 100 tons, kilograms, pounds, grams, or grains of mercury will give 108 tons, kilograms pounds, grams, or grains, respectively of mercuric oxide—no more, no less If the atom of mercury be $\frac{100}{1000000000}$ milligram in weight, an atom of oxygen will weigh $\frac{8}{1000000000}$ milligram We do not know the actual weights but we do know the relative weights If one atom could be actually weighed, the Tables of Atomic Weights would enable the weight of an atom of any other element to be calculated

The history of the atomic hypothesis —The ancient philosophers of the East—India, Greece, Italy, etc.—made many quaint guesses at the constitution of matter Among these guesses we find one taught by Kanada (the founder of a system of Hindu philosophy) long prior to the rise of Grecian philosophy The same guess was made by Democritus, Leucippus, and Lucretius, and their guess lives, more or less modified, in modern chemistry These philosophers seem to have taught (1) matter is discrete (2) all substances are formed of atoms which are separated from one another by void space, (3) the atoms are in constant motion, and (4) motion is an inherent property of the atoms The atoms were supposed to be too small to be perceived by the senses, and they were further supposed to be eternal, indestructible, and unchangeable Atoms differed from each other in shape, size and mode of arrangement, and the properties of all substances were supposed to depend upon the nature of the constituent atoms and the way the atoms were arranged So far as the experimental evidence available to the Grecian philosophers in support of this particular guess is concerned, its long life—in the form of the chemist's atomic theory—can only be attributed to chance The modern theory, unlike the old speculation, is based upon the observed laws of chemical change, and it cannot stand apart from them

Many thinkers—Francis Bacon, Réné Descartes, Pierre Gassendi, Robert Boyle, Robert Hooke, John Mayow, etc —were more or less partial to a theory of atoms. Isaac Newton (1675) tried to explain Boyle's law on the assumption that gases were made up of mutually repulsive particles, and the above quotation shows that he also referred chemical changes to different associations of the atoms M W Lomonossoff, also, had a fairly clear concept of the atomic structure of matter in 1748, while Bryan Higgins (1776) and William Higgins (1789) explained the constant composition of salts, with more or less confidence, in terms of the atoms Bryan Higgins appears to have held the view that two different atoms combine in the proportions of 1 1, and in that proportion only, while William Higgins imagined a combination in multiple

not so sure about It is also conceivable that at some future time it may be necessary to extend the diagram upwards and to the right A similar diagram for the compounds of carbon and hydrogen indicates scores of known compounds

proportions, but believed that the combination 1 : 1 was the most stable.

Dalton's atomic hypothesis.—It is thus impossible to say who invented the atomic theory, because it has grown up with chemistry itself. In the work of William Higgins the hypothesis was little more than an inanimate doctrine. It remained for Dalton to quicken the dead dogma into a living hypothesis. John Dalton (1801) employed the atomic hypothesis to explain the diffusion of gases, and later (1803) based an hypothesis of the structure of matter and of chemical combination upon the following postulates, which may be regarded as a very brief statement of the so-called Dalton's atomic theory:

1. Atoms are real discrete particles of matter which cannot be subdivided by any known chemical process.
2. Atoms of the same element are similar to one another, and equal in weight.
3. Atoms of different elements have different properties—weight, affinity, etc.
4. Compounds are formed by the union of atoms of different elements in simple numerical proportions—1 : 1, 1 : 2, 2 : 1, 2 : 3, etc.
5. The combining weights of the elements represent the combining weights of the atoms.

The hypothesis of Dalton respecting atoms, and more particularly atomic weights, is not quite that which prevails in modern chemistry.

The defect in Dalton's atomic theory.—According to the atomic theory, an atom is the smallest particle of an element which can enter into or be expelled from chemical combination.[1] How is the "smallest combining weight" of an atom to be fixed? In carbon monoxide, for example, we have oxygen and carbon in the following proportions by weight:

$$\text{Oxygen} : \text{Carbon} = 8 : 6$$

and in carbon dioxide

$$\text{Oxygen} : \text{Carbon} = 8 : 3$$

What is the atomic weight of carbon if the atomic weight of oxygen is 8? Obviously, the evidence now before us would be consistent with many different views. Carbon monoxide may be a compound of one oxygen atom with two carbon atoms each with a combining weight of 3; or a compound of one oxygen atom with one carbon atom with a combining weight of 6. In the latter case, carbon dioxide is a compound of one carbon atom combining weight 6 with two oxygen atoms, and the same combining weights would have been obtained if any number n of carbon atoms were combined with $2n$ oxygen atoms. Similar difficulties arise when we apply the idea of atoms so far developed to other combinations of the elements. There is, therefore, some confusion. The concept of the atom becomes more or less indistinct and vague when the attempt is made to develop a consistent system on the basis of the atomic hypothesis as propounded by Dalton. Dalton's theory is defective because it lacks a standard for fixing the atomic weights of the different elements.

It may be perfectly true, as Lord Kelvin has pointed out, that "the assumption of atoms can explain no property of a body which has not previously been attributed to the atoms," but the assumption has none

[1] If we think of the derivation of the word *atom*—from the Greek α, not; τέμνω (temno), I cut—"that which cannot be subdivided" we must add "chemically." But our definition of the atom says nothing about subdivision nor about the ultimate nature of the atom. The term "atom" was once used to represent the "smallest interval of time," a "moment."

the less proved an invaluable aid in forming mental concepts of the different phases of a chemical reaction, and it has enabled chemists to successfully anticipate the results of experimental research A R A. Smith said in 1884 "We believe in atoms because so far as we can see, nature uses them" The greater the number of facts consistently explained by one and the same theory, the greater the probability of its being true. The overwhelming mass of circumstantial evidence, direct and indirect, which modern chemistry and physics offers, has justified the faith of Dalton, and almost, but not quite, demonstrated the real existence of tangible atoms

§ 12 The Language of Chemistry.

> However certain the facts of any science however just the ideas derived from these facts, we can only communicate false or imperfect impressions to others, if we want words by which these may be properly expressed — A L Lavoisier

The nomenclature of a science, that is, the group of technical terms peculiar to that science is of vital importance. It is virtually impossible to separate the nomenclature from the science itself Lavoisier emphasized the importance of this in his classical *Traite Elementaire de Chimie* (1789) Every science consists of three things (1) the facts which form the subject-matter, (2) the ideas represented by those facts, and (3) the words in which those ideas are expressed "Like three impressions of the same seal, the word ought to produce the idea; and the idea ought to be a picture of the fact "

Special technical words are employed to fix and describe the ideas and principles of chemistry—as of all other sciences Technical terms should be precise and clear, and not tainted with ambiguity and vagueness Such technical terms form part of the current language of chemistry. However strange the terms may appear at first they soon grow familiar to the ear, and they can then be used without effort W. Whewell has pointed out, very aptly, that "technical terms carry the results of deep and laborious research They convey the mental treasures of one period to the generations that follow, and laden with this, their precious freight, they sail safely across the gulfs of time in which empires have suffered shipwreck, and the language of common life has sunk into oblivion"—witness many of the terms used in the chemistry of to day were coined by the early Arabian chemists

Naming the elements.—A great number of the elements have been christened with names derived from Greek roots *E g*, *iodine*—from its violet vapour, *chlorine*—from its green colour, *chromium*—from the colour of its compounds, *rhodium*—from the rose colour of its salts, *osmium*—from its smell, *helium*—from its occurrence in the sun, *argon*—from its indifference to chemical reagents, etc Other elements have been named more or less capriciously, thus some elements are named after particular localities—*strontium*, from Strontian (in Scotland), *ruthenium*, from Ruthenia (Russia), *yttrium*, *ytterbium*, *erbium*, and *terbium* are all derived from Ytterby (in Sweden), *palladium* is a name given in honour of the discovery of the planetoid Pallas, *uranium* in honour of the discovery of the planet Uranus, *beryllium* is derived from the name of the mineral beryl, *zirconium*, from the mineral zircon, *platinum*, from

the Spanish "plata," silver; *victorium*, from Queen Victoria; *thorium*, from "Thor," the son of Odin, a god in Scandinavian mythology; *vanadium*, from a Scandinavian goddess, Vanadis; *tantalum*, from Tantalus in Grecian mythology; and *niobium*, from Niobe, daughter of Tantalus.

Symbols.—The old alchemists used to represent different substances by symbols. For example, gold was represented by the symbol ⊙ or ☀, for the sun; silver, by ☾, the moon; etc. Lavoisier used the symbol ▽ for water;  for oxygen; etc. Dalton made a step in advance by representing *the atoms of the elements by symbols, and combining these symbols so as to show the elements present in a compound.* Thus, ⊙ represented hydrogen; ○ oxygen; ● carbon; etc. Water was represented by ⊙○; carbon monoxide by ○●; carbon dioxide by ○●○; etc. These symbols have all been abandoned. They are too cumbrous. To-day we follow J. J. Berzelius' method, suggested in 1811, and use one or two letters from the recognized name of the element to represent any particular element.[1] Thus, O represents oxygen; H, hydrogen; C, carbon; N, nitrogen; Cl, chlorine; etc. The names of ten elements start with C, and to prevent the possibility of confusion, a second leading letter is selected either from the name, or from the alternative Latin name of the element. Thus, C (carbon), Cb (columbium), Ca (calcium), Cd (cadmium), Ce (cerium), Cl (chlorine), Co (cobalt), Cr (chromium), Cs (cæsium), and Cu (cuprum, copper). The elements with alternative Latin names are symbolized: Sb for antimony (Lat. stibium); Cu for copper (Lat. cuprum); Au for gold (Lat. aurum); Fe for iron (Lat. ferrum); Pb for lead (Lat. plumbum); Hg for mercury (Lat. hydrargyrum); K for potassium (Lat. kalium); Na for sodium (Lat. natrium); and Sn for tin (Lat. stannum).

Naming the compounds.—Each element forms with other elements a group of compounds which are said *to contain* the respective elements, because the elements in question can be obtained unchanged from the compounds. **Consequently every compound has an elementary or ultimate composition.** Compounds are symbolized by joining together the letters corresponding with the different elements in the compound. Thus, HgO represents mercury oxide, a compound of mercury and oxygen. When only two elements are united to form a compound, the name of the second element is modified so that it ends in ide.

The symbol for the element also represents one of its atoms. If more than one atom is present in a compound, a small figure is appended to the bottom[2] right-hand corner of the symbol for an atom of the element, to indicate the number of atoms present. Thus "H_2O" represents a molecule of water, *i.e.* a compound containing two atoms of hydrogen and one of oxygen; "CO" represents a molecule of carbon monoxide—a compound containing one atom of carbon and one atom of oxygen; "Na_2CO_3" represents a molecule of sodium carbonate—a compound containing two atoms of sodium, one atom of carbon, and three atoms of oxygen. A letter affixed in front of a group of symbols represents

[1] Unfortunately some elements have not yet been christened with a name recognized by all. Niobium—symbol Nb—and columbium—symbol Cb—are two different names for one element; glucinum—symbol Gl—and beryllium—symbol Be—are two different names for another element.

[2] In France, generally at the top.

the number of times that group occurs in the given compound Thus crystallized sodium carbonate is symbolized, $Na_2CO_3.10H_2O$. This means that this compound contains the equivalent of one Na_2CO_3, and ten equivalents of the group H_2O

Compounds of one element with oxygen are called oxides, and the process of combination is called **oxidation** When an element forms more than one oxide, a Greek numerical suffix is often prefixed to the word "oxide" Thus, SO_2 is sulphur dioxide, SO_3, sulphur trioxide; CO, carbon monoxide, CO_2, carbon dioxide, PbO, lead monoxide; PbO_2 lead dioxide or lead peroxide

Some of the commoner prefixes are

	1	2	3	4	5	6
Latin	Uni-	Bi-	Ter-	Quadri	Quinque	Sexa-
Greek	Mono	Di-	Tri-	Tetra-	Penta-	Hexa-

	7	8	9	10	11	12
Latin	Septa	Octo	Novem	Decem-	Undecem	Duodecem
Greek	Hepta-	Octo	Ennea-	Deka	Endeka-	Dodeka-

	Half	Whole	Equal	Many
Latin	Semi-	Omni	Equi-	Multi-
Greek	Hemi-	Holo-	Homo-	Poly-

It is considered bad style to mix Latin and Greek root words and prefixes. Consequently we usually try to keep Greek with Greek, and Latin with Latin Thus, we say "diatomic," not "biatomic", "bimolecular," not "dimolecular", "bivalent," not "divalent"; and "bivariant," not "divariant", because "atomic" is derived from a Greek word, while "molecular," "variant," and "valent," are derived from Latin words There are, however, many hybrids universally recognized *E g*, millimetre, centimetre, etc Monovalent, divalent, etc, are also used at times in spite of their hybrid character We cannot, therefore, always be "purists" without defying custom, which, as Horace has said, decides the language we must use

Sometimes the termination -ic is affixed to the name of the metal for that oxide which contains the greater proportion of oxygen, and -ous for the oxide containing the lesser proportion of oxygen [1] For instance, SnO is either stannous oxide, or tin monoxide, FeO is ferrous oxide, and Fe_2O_3 ferric oxide The last-named method of naming the compounds is not always satisfactory when the elements form more than two compounds To get over the difficulty, a prefix hypo (meaning "under," or "lesser") is sometimes added to the compound containing the least, and per- ("beyond," "above") is added to the one with the most oxygen Thus,

Persulphuric acid	$H_2S_2O_8$	Perchloric acid	$HClO_4$
Sulphuric acid	H_2SO_4	Chloric acid	$HClO_3$
Sulphurous acid	H_2SO_3	Chlorous acid	$HClO_2$
Hyposulphurous acid	$H_2S_2O_4$	Hypochlorous acid	$HClO$

The six nitrogen oxides—nitrogen monoxide, dioxide, trioxide, tetroxide, pentoxide and hexoxide—would be awkwardly named by this system

[1] For historical reasons, the names of some compounds do not conform to this system because the affix "ic" was assigned to the compound first discovered, and the compounds subsequently discovered were named accordingly

Oxides like alumina—Al_2O_3, ferric oxide—Fe_2O_3, etc., are sometimes called *sesquioxides* (Latin, *sesqui*, one half more)[1]

The nomenclature of inorganic chemistry is thus based upon the principle that the different compounds of an element with other elements can be named by a simple change in the beginning or termination of the word—witness ferric and ferrous oxides, and also by the addition of a numerical suffix showing the relative number of atoms of the corresponding element in its compounds These little artifices, apparently trivial, are really important advances in the language of chemistry The method has some defects, but when the necessity for a modification becomes acute, it will probably not be difficult to change Language generally lags in the wake of progress.

Questions

In the questions appended to this and subsequent chapters, I have omitted direct "quiz" questions such as "What is the symbol of hydrogen?" "How is hydrogen prepared?" etc Questions of this kind have a certain value in revision work, and good sets will be found in the brochure published as an "Appendix for Newth's Inorganic Chemistry", in H P Talbot's "Study Questions—Inorganic Chemistry and Qualitative Chemical Analysis" and in F Jones' "Questions on Chemistry" Most of the questions here reproduced involve a little thought or work of comparison, and they will accordingly serve to emphasize special features which different examiners have thought to be important Socrates long ago demonstrated the value of questions as an auxiliary in clarifying hazy notions

1 Name two important respects in which metals differ from non metals Name an element which may be regarded both as metal and as non metal, and give some of the reasons —*Princeton Univ, U S A*

2 When substances are brought into contact, how would you know whether they acted chemically on one another, or simply remained mechanically mixed? Describe minutely in illustration the combination of any two elements —*Oxford Junior Locals*

3 Distinguish as clearly as you can between changes in matter which are classed as chemical and those classed as physical Which of the following do you think are chemical, and which are physical (*a*) freezing ice cream (*b*) souring milk, (*c*) burning a candle (*d*) distilling water, (*e*) magnetizing iron, (*f*) electrolysis of a solution of copper sulphate

4 Give a brief outline of the atomic theory, together with its history —*Princeton Univ, U S A*

5 Show how the facts summarized in the law of multiple proportions are explained by the atomic theory Two oxides of a metal M contain respectively 22 53 and 30 38 per cent of oxygen If the formula of the first oxide be MO what will be that of the second?—*Sheffield Univ*

6 In what relations do the elements stand to other single homogeneous substances, and such substances to other natural or artificial objects? Refer for illustration to quicksilver, water, gunpowder, a piece of granite, an orange, a picture —*New Zealand Univ*

7 State the law of multiple proportions How would you proceed to prove the law experimentally?—*Aberystwyth Univ*

8 John Dalton expressed and helped to establish the law of multiple proportions, and he also proposed an atomic theory Explain why one of these contributions to chemical science was classed as a law while the other was not —*American Coll*

9 Define the Laws of Definite and Multiple Proportions Show how the

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[1] The oxides can be roughly divided into two classes Some oxides, with water, form acids, and others act as bases It is not very easy, at this stage of our work, to draw a sharp line of demarcation between the two The *acidic oxides* have a sour taste, and turn a solution of blue litmus red, the *basic oxides* turn a solution of red litmus blue, and have a soapy feel.

following analyses of three oxides of nitrogen illustrate the Law of Multiple Proportions —

	A	B	C
Nitrogen	63 65	46 68	25 94
Oxygen	36 35	53 32	74 06

Victoria Univ Manchester

10 Define a chemical change Give instances of chemical changes occurring in nature Describe experiments which show that matter is not lost in chemical changes —*Owens Coll*

11 Amplify the quotation "Before everything a man of science should aim at being definite, clear, and accurate"

12 Describe *in detail* how you would separate the constituents of ordinary black gunpowder and ascertain the percentage in the mixture of each constituent —*St Andrews Univ*

CHAPTER III

Water and Hydrogen

§ 1 Hydrogen—Preparation and Properties

History—It has been known for a very long time that an air or gas is produced when iron is dissolved in dilute sulphuric acid. T B Paracelsus, in the sixteenth century, described the action somewhat quaintly He said that when the acid acts on iron "an air arises which bursts forth like the wind." J B van Helmont (c 1609) described this gas as a peculiar variety of air which was combustible and a non supporter of combustion, but his ideas were somewhat hazy, for he confused hydrogen with other gases, like methane and carbon dioxide, which do not support combustion. Priestley, and writers generally up to about 1783, used "*inflammable air*" as a general term to include this gas, as well as the hydrocarbons, hydrogen sulphide, carbon monoxide, and other combustible gases. H. Cavendish (1766) showed that the inflammable air produced by the action of dilute sulphuric or hydrochloric acid on metals like iron, zinc, and tin was a distinct definite substance, and A. L. Lavoisier (1783) called the gas "hydrogen"

The gas obtained from metallic iron is not very pure, and it possesses a distinct smell owing to the presence of hydrocarbon gases, etc, formed by the action of the acid on the carbon compounds associated, as impurities, with commercial iron The solution remaining after the action of sulphuric acid on the iron when put aside in a cool place soon forms beautiful pale green crystals of ferrous sulphate Their mode of formation, etc, is quite analogous with the process used in the preparation of zinc sulphate crystals, Fig 4. Magnesium and aluminium furnish a fairly pure gas, with aluminium the acid should be warmed to start the reaction In these cases not only is hydrogen gas obtained, but crystals of magnesium sulphate and of aluminium sulphate can be obtained from the liquids in which the metals have been dissolved. The action of the acid on tin is rather slow, granulated zinc is used for general laboratory work, in the following manner

Preparation in the laboratory—Granulated zinc is placed in a two-necked Woulfe's bottle,[1] *A*, Fig 9 One neck is closed air tight by a one-hole rubber stopper fitted with a funnel tube, *B*, extending nearly to the bottom of the bottle, the other neck is fitted with a glass tube, *C*—delivery tube—bent as shown in the diagram The delivery tube dips

[1] The tubulated bottles for washing gases appear to have been first described by Peter Woulfe in 1784, hence the term Woulfe's bottles, not "Woulff's bottles"

under the beehive, *D*, placed in a basin of water, *E* The vessels *D* and *E* form a collecting, gas, or pneumatic trough [1]

Pour some water through the funnel tube until the zinc is well covered, make sure that all the joints are air-tight, and that no escape of gas is possible other than through the delivery tube Pour concentrated sulphuric acid, a little at a time, through the funnel tube until the gas begins to come off vigorously The mixture of air and hydrogen gas first issuing from the delivery tube is very explosive. It is therefore necessary to make sure that all the air has been expelled before the hydrogen is collected in the gas cylinders, or gas jars, *F* Hence, invert a test tube full of water over the hole in the upper floor of the "beehive" When the tube is full of gas, apply a lighted taper to the mouth of the test tube If the gas detonates, repeat the trial until the gas burns quietly Fill a gas jar full of water, cover it with a greased glass plate, *G*, turn the jar and cover upside down, and remove the plate while the mouth of the gas jar is below the surface of the water in the gas trough Place the mouth of the jar over the hole in the floor of the "beehive" When the jar is full of gas, close the mouth of the jar with the glass plate and remove the vessel from the collecting trough Stand the jar mouth downwards, and collect several jars of gas in a similar way

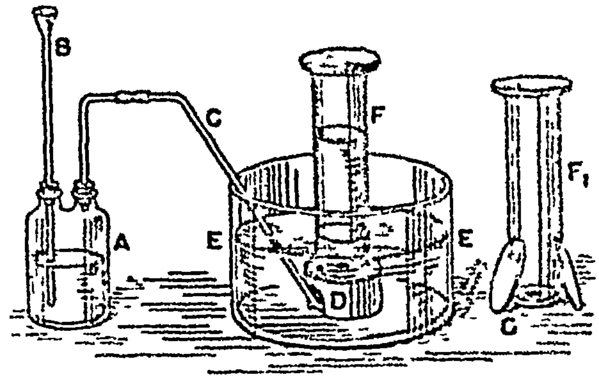


Fig 9 —The Preparation of Hydrogen

Properties —Plunge a lighted taper into a jar of the gas held mouth downwards, the gas is combustible, for it burns with a scarcely visible blue flame at the mouth of the jar, and the taper is extinguished, showing that the gas is a non-supporter of combustion The gas can be poured upwards from one jar to another as illustrated in Fig 10, and it can be proved that the gas has actually been transferred from the one vessel to the other by testing the contents of each jar with a lighted taper The gas is therefore lighter than air, indeed, for many purposes there is no need to use the pneumatic trough for collecting hydrogen Bring the gas jar mouth downwards over a jet of hydrogen The hydrogen collects at the top of the jar, and displaces the air downwards—hence the term collecting gases

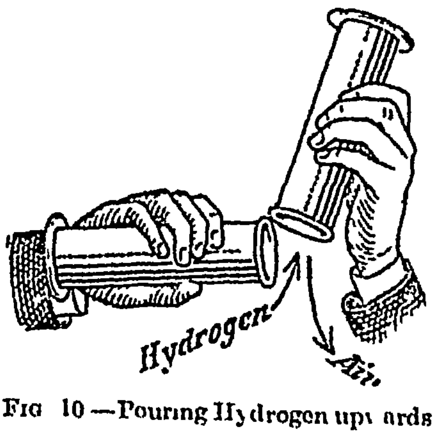


Fig 10 —Pouring Hydrogen upwards

[1] The discovery of the water pneumatic trough is often attributed to Stephen Hales, about 1730, J Priestley afterwards used mercury in place of water and this enabled him to manipulate gases soluble in water

by the downward[1] displacement of air Later on we shall meet another important gas which turns clear lime water turbid—hydrogen does not As indicated above, a mixture of hydrogen with oxygen or air is violently explosive. This can be illustrated by mixing two volumes of hydrogen gas with either one volume of oxygen or five volumes of air in a soda-water bottle. A lighted taper applied to the mouth of the bottle causes the gas to detonate violently The combustion of the whole mass is almost instantaneous.

These experiments have taught us that hydrogen is a colourless gas without taste or smell Its specific gravity is very low compared with air, in other words, hydrogen gas is lighter than air The gas is inflammable, and burns in air with an almost colourless flame, while a lighted taper is extinguished when plunged into the gas Hydrogen gas has no apparent action on clear lime water

§ 2 Burning Hydrogen in Air

Fill a gas holder,[2] *M*, Fig 11, with water Close the two stopcocks, remove the stopper *N* and place the delivery tube from the hydrogen apparatus (Fig 9) in the opening Water is displaced[3] by the hydrogen When full, close *N* with the stopper By keeping the large funnel, *F*, filled with water, and regulating the two stopcocks, *S* and S_1, hydrogen can be dis placed from the gas holder at any re quired speed[4] Connect a glass tube, bent as shown in the diagram, with the exit tube from the gas holder, interposing a calcium chloride tower *G*, packed with granulated calcium chloride, and a plug of glass wool at each end. The object of this tube is to remove moisture from the gas.[5] Place a bell jar, *K*, in a dish of distilled water, *H*,

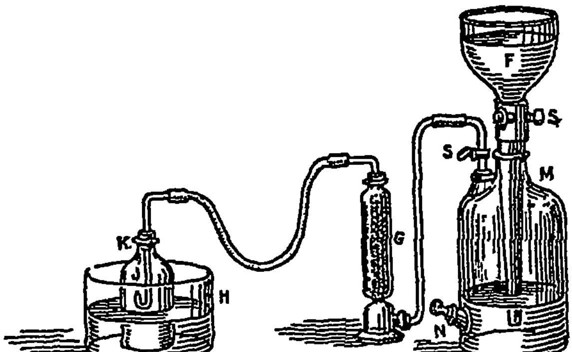


Fig 11 —The Action of burning Hydrogen in Air

[1] Many writers call this *collecting the gas by upward displacement* The student must therefore make perfectly clear there is no confusion in his own use of the term

[2] There is no special need for a gas holder in this particular experiment Kipp's apparatus may be used, as illustrated in *A*, Fig 12 The gas holder is introduced here to illustrate one of the methods of storing gases in the laboratory

[3] This is done over a sink to carry off the surplus water

[4] When hydrogen is to be burned a jet of hard glass should be used, or, better, a tip of platinum or a piece of quartz glass tubing should be attached by a piece of rubber tubing to the delivery tube The hydrogen flame is very hot and soon melts ordinary soft glass

[5] Concentrated sulphuric acid is also frequently used to absorb moisture from gases Phosphorus pentoxide is used in special cases where a very powerful absorbent is needed for very small amounts of moisture The drying agent used must not react with the gas

Fig 11, and arrange the delivery tube *J* so that it can be quickly fixed as illustrated in the diagram Collect a test tube of the gas by downward displacement as it leaves the exit tube in order to make sure that all air has been displaced from the tubes

When the test is satisfactory, light the jet of hydrogen, and adjust the flame until it is about the size of a candle flame, lower the burning jet into the cylinder of air as shown in Fig 11 Note that the water rises in the jar, and that the flame of hydrogen gradually expires Immediately this occurs, stop the current of hydrogen by means of the stopcock, otherwise hydrogen gas will pass from the gas holder and mix with the residual air

The gas remaining in the jar has quite similar properties to the gas remaining after mercury is calcined in air, p 10 Consequently, it is inferred that when hydrogen burns in air, it unites with the oxygen and leaves nitrogen behind If the experiment be carefully done, four-fifths of the original volume of air remain The burning hydrogen removes one fifth of the original volume of air Hydrogen does not burn in the residual nitrogen

A certain amount of "dew" collects on the inner walls of the bell jar, but that, of course, *may come from the* water in the dish below In fine, we have reasons for supposing that hydrogen, in burning, combines with oxygen to form an oxide of hydrogen in the same sense that mercury, when calcined in air, combines with oxygen to form mercuric oxide It remains to try and isolate the hydrogen oxide whose existence we have just inferred, but not proved

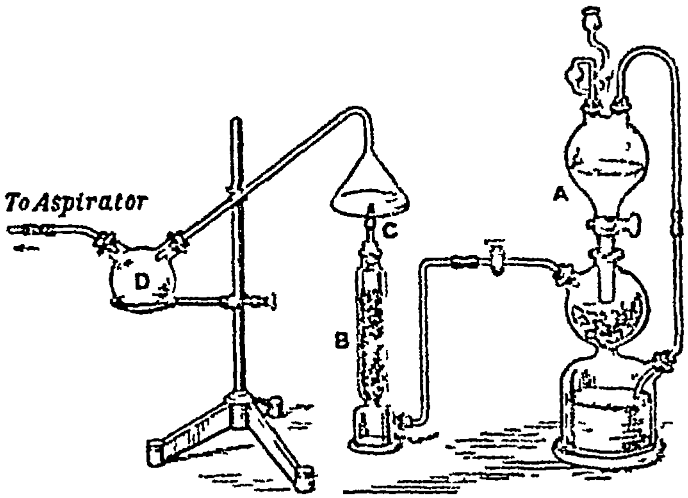


FIG 12 —The Synthesis of Water

Fit up the apparatus previously described for the preparation of hydrogen, Fig 11, or use one of the numerous modifications of Kipp's apparatus, say, *A*, Fig 12 Kipp's apparatus is very convenient when a steady current of hydrogen is needed for some time, or when variable quantities of gas are required intermittently [1] The Kipp's apparatus may conveniently be used instead of the gas holder in the preceding experiment. Connect the Kipp's apparatus with the drying tower packed with calcium chloride, *B*, and fitted with a jet *C*, for burning the hydrogen A piece

[1] Zinc is placed in the middle bulb, and dilute sulphuric acid (1 vol acid, 8 vols water) or hydrochloric acid in the lower and upper bulb, as shown in the diagram Open the stopcocks until the gas has displaced the air The velocity of the current of gas is regulated by the stopcocks When the stopcock is closed, the acid is forced away from the gas The side tube helps to prevent an accumulation of spent acid near the zinc There are over a hundred modifications of the principle for supplying a continuous stream of gas

of narrow quartz glass tubing makes an excellent jet. If this is not available, use a jet of hard "combustion" glass tubing Test the gas, to ensure the absence of air, by bringing a *dry* test tube over the jet of gas issuing from the drying tower Bring a lighted taper to the mouth of the tube. The hydrogen should burn quietly, in that case, it will be noticed that a kind of "dew" collects on the inside of the test tube. Bring the jet of burning gas under the inverted funnel fitted, as shown in the diagram, with a bulb, *D*, connected with an aspirator for sucking a gentle current of air through the bulb The current of air carries along the products of combustion from the hydrogen flame A clear colourless liquid collects in the bulb [1] This liquid has all the properties of water—clear, colourless, tasteless, no smell, freezes at 0°, boils at 100°, etc It is therefore provisionally inferred that **water is a hydrogen oxide formed when hydrogen burns in air**

§ 3 Morley's Experiment on the Composition of Water by Weight.

E W Morley (1895) has a very fine application of the principle underlying this experiment Known weights of pure dry hydrogen and pure dry oxygen were stored in two large glass globes.[2] The globe containing oxygen was connected with *C*, Fig 13 The oxygen passed through a layer of phosphorus pentoxide,[3] and thence into the glass chamber *M* *viâ* one of the jets *A*, the globe containing hydrogen was similarly connected with another tube, *D*, containing phosphorus pentoxide, and the hydrogen led into the chamber *M* *viâ* one of the jets *A* The rates at which the gases enter the chamber was regulated by suitable stopcocks. The chamber *M* was previously evacuated and weighed. One of the gases, say oxygen, was allowed to enter *M*, and electric sparks were passed across the terminals *F* just over the jets *A* Hydrogen was led into the apparatus and ignited by the sparks. The rates at which hydrogen and oxygen entered the chamber were regulated so that the formation of water was continuous. The water formed was condensed, and collected in the lower part of the chamber To hasten the condensation, the apparatus was placed in a vessel of cold

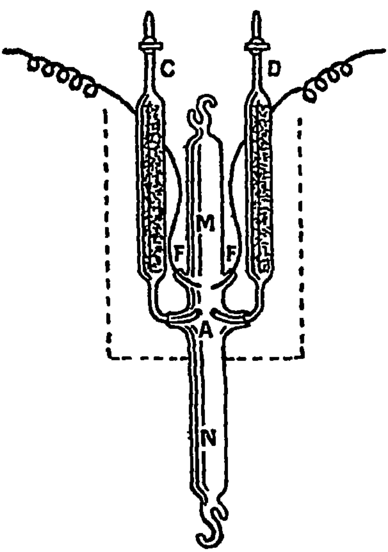


FIG 13.—Morley's Experiment — Synthesis of Water

[1] The bulb can be cooled, if desired, by resting it in a funnel, and allowing water to run over the bulb and out from the bottom of the funnel to the sink

[2] The hydrogen was prepared by heating palladium hydride, and the oxygen by heating potassium chlorate The apparatus for storing and drying the hydrogen and oxygen is not shown in Fig 13

[3] The phosphorus pentoxide is not intended to dry the *entering* gases—these have already been dried

water—dotted in the diagram. When a sufficient amount of water was formed the apparatus was placed in a freezing mixture. The mixture of unconsumed oxygen and hydrogen remaining in the tube, was pumped away, and analysed. The weights of hydrogen and oxygen so obtained were added to the weights of unconsumed hydrogen and oxygen remaining in the globes. The phosphorus pentoxide tubes prevented the escape of water vapour. The amount of water formed was determined from the difference in the weights of the system *M* before and after the experiment. The amounts of hydrogen and oxygen used were determined from the weights of the corresponding globes before and after the experiment. The amount of water formed was determined from the increase in the weight of the above-described vessel before and after the combustion. Morley, as a mean of eleven experiments, found that

Hydrogen used	3.7198 grams
Oxygen used	29.5335 grams
Water formed	33.2530 grams

Hence, taking oxygen = 16 as the unit for combining weight, it follows that 16 *parts by weight of oxygen combine with* 2.016 *parts by weight of hydrogen to form* 18.016 *parts of water*—within the limits of the small experimental error.

§ 4. Dumas' Experiment on the Composition of Water by Weight.

Hydrogen does not combine easily with many of the elements, but it readily combines with oxygen, chlorine, fluorine, lithium, and a few others. Hydrogen will very often remove oxygen and chlorine from their compounds with the other elements. Thus, when hydrogen is passed over hot ferric oxide, lead oxide, nickel oxide, copper oxide, etc., the hydrogen combines with the oxygen of the oxide and leaves behind the metal. In these experiments, the hydrogen is said to be *oxidized*, and the metallic oxide, *reduced*.

If a known amount of copper oxide be employed, and the water formed be collected and weighed, the weight of the reduced copper oxide will show how much oxygen has been used in forming a definite amount of water. This was done by J. B. A. Dumas in 1843. His experiment is not the best of its kind, although it was the best of its time, and it has long held an honoured place in chemical text books. The experiment illustrates some important principles, and it is therefore here described in outline.

The preparation of pure hydrogen.—The hydrogen was prepared by the action of zinc on sulphuric acid. It might be thought that pure zinc and pure sulphuric acid should be used. Experiment shows, curiously enough, that the action is so very, very slow, that it is often stated that "absolutely pure sulphuric acid, even when diluted with pure water, has no action on perfectly pure zinc." Moreover, it is exceedingly difficult to prepare pure zinc and pure sulphuric acid. Hence, pure reagents were not used for the preparation of the hydrogen. Accordingly, the gas may contain nitrogen and oxygen derived from the air, sulphur dioxide and hydrogen sulphide derived from the reduction of the sulphuric acid by the hydrogen, carbon dioxide, arsenic hydride (if the acid or the zinc contained arsenic), hydrogen phosphide (if the zinc or the acid contained phosphorus), nitrogen oxides (if the acid contained nitrogen oxides), and water vapour.

Accordingly, Dumas (1842) used sulphuric acid, which had been well boiled, to get rid of dissolved air, and then passed the hydrogen through a series of U-tubes—Fig 14—containing (1) pieces of glass moistened with lead nitrate to remove hydrogen sulphide, (2) solution of silver sulphate to remove arsenic and phosphorus compounds, (3) solid potassium hydroxide to remove sulphur dioxide, carbon dioxide, and nitrogen oxides,[1] and (4) phosphorus pentoxide to remove moisture[1] not absorbed by the solid potassium hydroxide. The phosphorus pentoxide tubes were placed in a freezing mixture The tube marked (5) in the diagram contained phosphorus pentoxide It was weighed before and after the experiment. If no change in weight occurred, it was assumed that the hydrogen passing through was quite dry

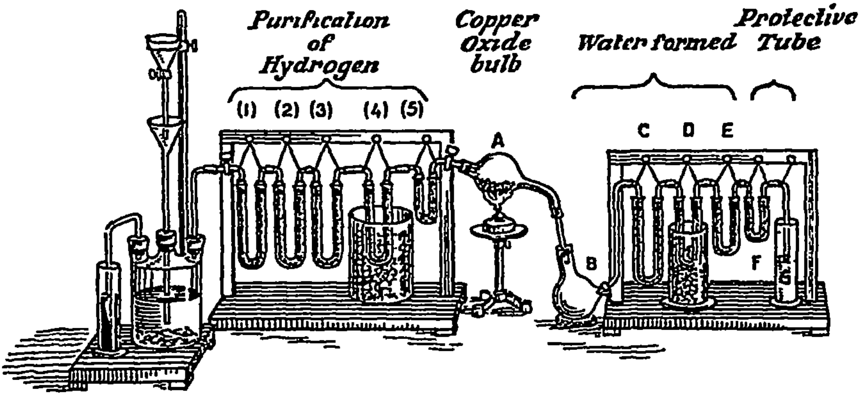


FIG 14 —Dumas' Experiment (abbreviated)

The experiment —The purified hydrogen was passed through a weighed bulb, *A*, containing copper oxide, and heated by the spirit lamp underneath Most of the water condensed in the bulb *B*, and the remainder was absorbed in the U-tube *C* containing solid potassium hydroxide, and in *D* and *E* containing phosphorus pentoxide The phosphorus pentoxide tube *D* was kept cool by a freezing mixture The three tubes *C*, *D*, *E*, and the bulb *B*, were weighed before and after the experiment The last U tube, *F*, containing phosphorus pentoxide was followed by a cylinder, *G*, of sulphuric acid through which hydrogen escaped. The vessels *F* and *G* were not weighed, they served to protect the other tubes from the external atmosphere

The results —The average of nineteen experiments by Dumas (1842) gave

Copper oxide lost in weight	44 22 grams
Water produced	49 76 grams
Hydrogen (by difference)	5 54 grams

Hence, every 16 parts by weight of oxygen combined with 2 004 parts by weight of hydrogen to form water The later determination of Morley gave 16 2 016 There is a curious error in Dumas' experiment which,

[1] Dumas used three potassium hydroxide tubes, and two phosphorus pentoxide tubes I have taken the liberty of showing only one of each in the diagram

if not corrected makes the result a little high. The reduced copper retains some hydrogen very tenaciously (see occlusion of hydrogen by the metals, p. 102). In approximate work we may take it that 2 parts by weight of hydrogen combine with 16 parts by weight of oxygen to form 18 parts of water.

§ 5 The Decomposition of Water by Metals

In the preceding experiments water has been synthesized from its elements. Let us now examine some methods of decomposing water into its elements—analysis. Fill an iron, porcelain, or hard glass tube—60 cm. long and 1.5 cm. diameter—with bright iron turnings or bright iron nails. In Fig. 15 a hard glass tube is used. This is drawn out at one end as shown in the diagram. This end is fitted with a delivery tube dipping in a gas trough. A roll of previously ignited asbestos paper, 6 cm. long, is inserted in the opposite end. This end is closed with a red rubber stopper and the exit tube of the flask so arranged that it passes a short distance into the core of the asbestos paper. The asbestos roll, later on, prevents the liquid water coming into contact with the hot glass and breaking the tube. Water is boiled in the flask and the steam passing through the red hot iron turnings, is decomposed. When all the air has been driven out of the apparatus hydrogen may be collected in the gas jar. The usual tests for hydrogen indicated on p. 44 may be applied.

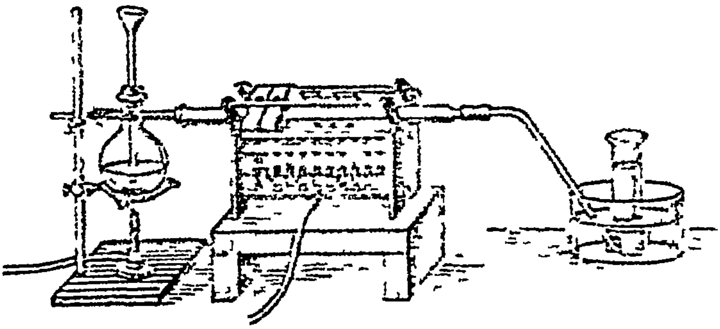


FIG. 15.—Decomposition of Steam by Hot Iron.

Lavoisier made a similar experiment to this in 1783, and stated that the metallic iron "is converted into a black oxide precisely similar to that produced by the combustion of iron in oxygen gas." The iron is oxidized by the water, and the water is reduced, forming "a peculiar inflammable gas," which Lavoisier named "hydrogen" because "no other term seemed more appropriate." The word signifies the "generative principle of water," from the Greek ὕδωρ (hydor), water, and γεννάω (gennao), I generate or produce. The German word for hydrogen is "Wasserstoff."

If zinc dust be used in place of iron, the temperature need not be much higher than the boiling point of water, since zinc reduces steam and forms zinc oxide at a comparatively low temperature. If a strip of magnesium ribbon be placed in a bulb of a hard glass tube and heated in a current of steam at a red heat, the metal appears to burst into flame, forming magnesium oxide. The resulting hydrogen can be ignited if the jet of steam be not too vigorous. Metallic calcium decomposes cold water and gives off hydrogen, but the action slows down very soon, probably because the calcium hydroxide is not all dissolved by the water, and in consequence a crust of this substance forms over the surface of the metal. The calcium

can be advantageously warmed with water in a flask, Fig 15, connected directly with a delivery tube leading to the gas trough. If the water is not free from carbonates, a crust of calcium carbonate also forms over the surface of the metal Calcium hydroxide is formed as well as hydrogen. Sodium decomposes cold water, giving off hydrogen, and forming sodium hydroxide The experiment is liable to unpleasant explosions when the sodium is confined so as to enable the resulting hydrogen to be collected. The following is an easy way of showing the action[1] A glass tube—4 or 5 cm long and 1 5 cm diameter, and open at both ends—is thoroughly dried inside This is lowered and clamped vertically in a dish of water so as not to wet the sides of the tube above the level of the water, Fig 16 A small piece of dry sodium, about 2 mm in diameter, is dropped into the tube. The hydrogen evolved can be lighted at the upper end of the tube. Sodium amalgam — that is, a solution of metallic sodium in mercury—decomposes water much less turbulently than sodium alone The result is similar when a small piece of potassium—3 or 4 mm diameter—is placed on water, but it reacts so violently that the temperature rises high enough to set fire to the hydrogen[2] This burns with a flame tinged violet, owing to the presence of the vapour of potassium, the hydrogen produced by the action of sodium on water burns with a yellow flame, owing to the contamination of the hydrogen by the vapour of sodium.

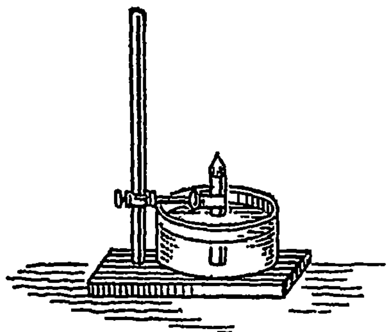


Fig 16 —The Action of Sodium on Water

This set of experiments gives a series of metals which appear to react with water with increasing violence, the metals seem to have an increasing "avidity" or "affinity" for oxygen

Iron, zinc, magnesium, calcium, sodium, potassium

§ 6 The Decomposition of Water by Electricity

W Nicholson and A. Carlisle, May 2, 1800,[3] happened to put a drop of water in contact with two wires from an electric battery and noticed the formation of small bubbles of gas about the tips of the wires when the tips of the wires were not in contact They then immersed the two wires in a glass of water, and found that gases were formed about both wires. They found the gas collected at one wire to be hydrogen, and at the other wire, oxygen Two volumes of hydrogen were collected for every volume of oxygen The gases were mixed and exploded The result was water This is very interesting We have seen that chemical combination can produce an electric current, here an electric current is used to produce chemical decomposition

The electrolysis of water —It will be convenient to modify Nicholson

[1] If there is an explosion no particular harm is done

[2] A sheet of plate glass should be held between the metal on the water and the operator

[3] J W Ritter noticed the decomposition of water by an electric current a year earlier—1799

and Carlisle's experiment. A trough, Fig 17 is half filled with water slightly acidulated with sulphuric acid Test-tubes full of acidulated water are placed in the position shown in the diagram over two plates of gold or platinum The plates are put in communication with an accumulator or galvanic battery[1] During the passing of the electric current, bubbles of gas from about the metal plates rise into the test-tubes. More gas is given off at one plate than the other The gas in each tube can be examined by means of a lighted taper or otherwise. In the one tube, the taper burns with the "blinding brilliance" characteristic of oxygen, and the gas in the other tube burns with the blue flame characteristic of hydrogen Some of the water has disappeared, but no change can be detected in the amount of sulphuric acid mixed with the water Hence it is inferred that the water, not the acid, has been decomposed The experiment succeeds equally well if a very dilute solution of sodium or potassium hydroxide be used with nickel or iron electrodes Here again the water, not the alkali, is decomposed. These reagents are used because

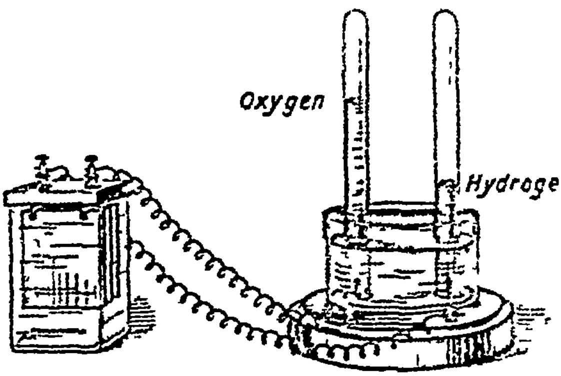


FIG 17 —Electrolysis of Water—Gases separated

FIG 18 —Electrolytic Gas

water alone does not conduct an electric current very well In fact, pure water is said to be a non conductor of electricity. Dilute solutions of acids or alkalies are good conductors. If iron electrodes are used in the acidulated solution, much of the oxygen formed during the decomposition of the water is used in oxidizing the metal

A mixture of one volume of oxygen and two volumes of hydrogen, called electrolytic gas or detonating gas, is often wanted in gas analysis, etc. This is easily provided by placing both electrodes under one receiver The apparatus illustrated in Fig 18 is often used for this work Electrolytic oxygen contains a little ozone and hydrogen peroxide if prepared by the electrolysis of acidulated water, but not if a solution of barium hydroxide be electrolyzed.

The formula for water used to be written HO when the atomic weight of hydrogen was taken unity, and oxygen 8 This agrees quite well with the determinations of Morley and of Dumas But we naturally ask for an explanation of the result of the electrolysis of water Does an atom of hydrogen occupy twice the volume of an atom of oxygen? This subject will be taken up in the next chapter

[1] There are scores of different ways of doing this experiment Some of the instruments are very ingenious, but easily broken

§ 7 Cavendish's Experiment on the Synthesis of Water by Volume

The older chemists considered water to be an element. They were quite right so far as their knowledge went, p 12, because they did not know how to decompose it into simpler substances. In the spring of 1781, J Priestley made what he called "a random experiment" to "entertain a few philosophical friends," in which a mixture of "inflammable air" with oxygen or atmospheric air was exploded in a closed vessel by means of an electric spark. The sides of the glass vessel were found "bedewed" with moisture after the explosion, but Priestley paid no particular attention to the phenomenon. H C Cavendish looked upon the deposition of the dew as a fact "well worth examining more closely" and immediately followed up the subject, in 1781, by exploding a mixture of "one measure of oxygen with two measures of inflammable air (hydrogen)" in a closed vessel No gas remained in the globe after the explosion, but the hydrogen and oxygen lost their gaseous form, and produced a certain weight of water The vessel and its contents underwent no change in weight, or parted with anything ponderable during the explosion, whilst a certain volume of gas was replaced by a certain weight of water Hence Cavendish deduced that liquid water consists, weight for weight, of the hydrogen and oxygen gases lost in its production Cavendish's results were communicated to Priestley and to Lavoisier not later than the summer of 1783, and published in 1784.[1]

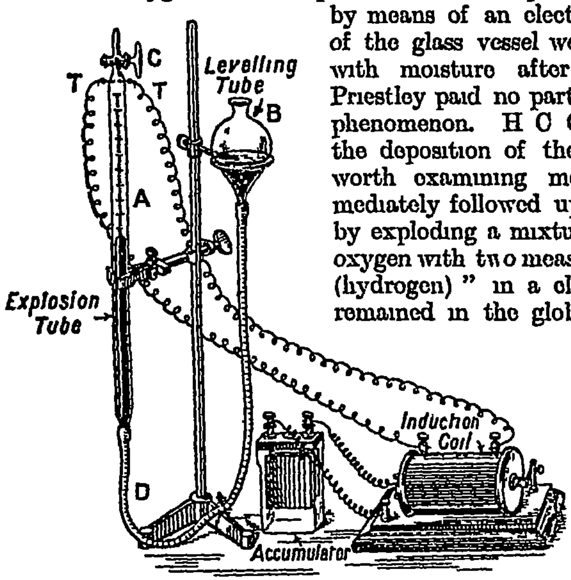


FIG 19 —Synthesis of Liquid Water by Volume

The experiment can be illustrated in the following manner A stout glass vessel, *A* is fitted with a stopcock, *C*, at one end, and with a piece of strong pressure tubing, *D*, connected with a reservoir at the other end, Fig 19 A pair of platinum wires, *T*, are sealed into the stout glass measuring vessel just below the stopcock. These wires are put in communication with an induction coil, which in turn is connected with an accumulator The tube *A* is called the eudiometer, or the explosion tube This is filled with mercury by adjusting the levelling tube *B* and the stopcock *C* A mixture containing one volume of oxygen and two volumes of hydrogen is introduced into the explosion tube *viâ* the stopcock *C* and by depressing

[1] James Watt, of engineering fame, expressed the *opinion*, in 1783, that Priestley's experiment meant that "water is composed of dephlogisticated air (oxygen) and inflammable air" There was much confusion about that time in the use of the term "inflammable air," and it is by no means clear that Watt meant by 'inflammable air" what we understand by "hydrogen" to day

the levelling tube When the explosion tube is about half or three fourths filled read the volume of its contents by bringing the mercury to the same level in both levelling tube and explosion tube Then depress the levelling tube so that the mercury falls nearly to the bottom of the explosion tube Pass a spark from the induction coil through the wire terminals of the explosion tube The gases explode, and the level of the mercury is again adjusted after the apparatus has stood for a few minutes in order to regain the temperature of the room The mercury rises nearly[1] to the level of the stopcock[2]

Suppose the experiment be repeated a number of times with, say, one volume of oxygen and three volumes of hydrogen—one volume of hydrogen remains after the explosion, again try the experiment with two volumes of oxygen and two volumes of hydrogen — one volume of oxygen will remain uncombined after the explosion It is inferred, from this experiment, that **two volumes of hydrogen and one volume of oxygen combine to form water, and if an excess of either oxygen or hydrogen be present, the excess will remain uncombined after the reaction**

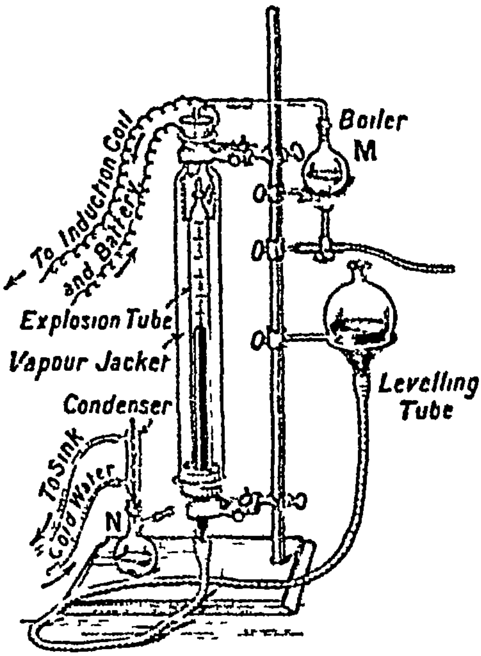


FIG 20 —Synthesis of Steam by Volume

Gas analysis —If a known volume of a gas containing hydrogen be mixed with an excess of air or oxygen, or if a known volume of a gas containing oxygen be mixed with an excess of hydrogen and exploded in a eudiometer, the contraction which occurs represents the volume of water formed, and the corresponding amount of the gas under investigation can be determined For example, 20 c c of air was mixed with 20 c c of hydrogen and exploded The mixed gases, after the explosion, occupied 28 c c Hence, the contraction was 12 c c Hence, 12 c c of the mixture combined to form water Of this two-thirds must have been hydrogen, and one third oxygen Hence, the original 20 c c of air contained 4 c c (*i e* one third of 12 c c) of oxygen This illustrates an important principle used in gas analysis

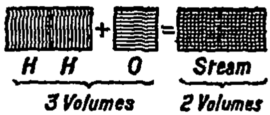
§ 8 The Volumetric Synthesis of Steam.

Let us modify the preceding experiment Place a hot vapour jacket about the explosion tube so that the water remains in the gaseous condition,

[1] The mixed gas probably contained a little air, and probably a slight excess of either oxygen or hydrogen

[2] The advantage of the forms of explosion vessel, Figs 19 and 20, lies in the fact that the explosion takes place under diminished pressure, and is not so liable to fracture the apparatus, because it is less violent

and does not condense to a liquid after the explosion The experiment is illustrated in Fig 20 The upper end of the glass jacket surrounding the explosion tube of Fig 20 is connected with a flask, *M*, containing toluene, boiling at about 110°, or amyl alcohol, boiling at about 130° The lower end of the jacket is connected with a flask and condenser *N*, so that the amyl alcohol can be recovered. When the amyl alcohol is steadily boiling, and the explosion tube has been filled as described in the preceding experiment, the gases are sparked In a few minutes, when the temperature has had time to adjust itself, bring the levelling tube in position for a reading It will be found that the steam occupies just two thirds the original volume of the mixed gases. Otherwise expressed,



Hence, it is inferred that when water is synthesized at a temperature above the point of condensation—100°—two volumes of hydrogen react with one volume of oxygen to form two volumes of steam It is necessary to correlate the different results described in this chapter when water is synthesized by volume and by weight.

Questions

1 50 c c of oxygen are mixed with 500 c c of hydrogen, both are measured at normal temperature and pressure, and an electric spark is passed through the mixture, what volume, if any, of gas will remain and how would you ascertain what it is?—*Science and Art Dept* Hint 50 c c of oxygen unite with 100 c c of hydrogen to form water, and most of the water condenses to a liquid, 400 c c of moist hydrogen remain

2 R Bunsen (1846) mixed 436 97 c c of dry air with hydrogen The mixed gases occupying 672 74, were sparked, and the residual gas, when dried, occupied 403 88 c c (*a*) What is the percentage composition of dry air, assuming the nitrogen of the air is not affected by the explosion? (*b*) Was sufficient hydrogen added to combine with all the oxygen of the air? Ansr (*a*) 20 91 per cent of oxygen and 79 09 per cent of nitrogen (*b*) Yes An excess of 58 20 c c of hydrogen was added

3 A mixture of 5 volumes of hydrogen and 3 volumes of air is surrounded by a hot jacket at a constant temperature of 110° What change of volume will occur after the mixture has been sparked, assuming that air contains 21 volumes of oxygen and 79 volumes of inert nitrogen? Here 3 vols of air contain 0 63 vol of oxygen, and 2 37 vols of nitrogen, 0 63 vol of oxygen unites with 1 26 vols of hydrogen to form 1 26 vols of steam Hence, the composition of the mixture after sparking will be 2 37 vols of nitrogen, 1 26 vols of steam, and 3 74 vols of hydrogen Total, 7 37 vols The volume of the original mixture is 8 vols Hence a contraction of 0 63 vol occurs This question could have been more simply answered by noting that the hydrogen simply removes 0 63 vol of oxygen from the mixture

CHAPTER IV

COMBINATION BY VOLUME

§ 1. Gay-Lussac's Law of Combining Volumes

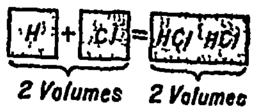
Thou hast ordered all things in measure, and number, and weight.—WISDOM OF SOLOMON.

NOT very long after Dalton had directed the attention of chemists to the relations subsisting between the weights of bodies which combine in different proportions, Gay-Lussac established a similar correspondence between volumes of combining gases. A. von Humboldt, the naturalist and explorer, collected samples of air from different parts of the world, and, with the aid of J. F. Gay-Lussac, analysed the different samples with the idea of finding if the composition of air was variable or constant. Gay-Lussac used Cavendish's process—explosion of a mixture of air and hydrogen gas (p. 52). As a preliminary, Humboldt and Gay-Lussac investigated the proportion by volume in which hydrogen and oxygen combine, and found the ratio of hydrogen to oxygen, by volume, to be nearly as 2 : 1. If either hydrogen or oxygen was in excess of these proportions, the excess remained, after the explosion, as a residual gas. Humboldt and Gay-Lussac (1805) found:

Vols. oxygen	Vols. hydrogen	Vols. residue
100	300	101.3 hydrogen
200	200	101.7 oxygen

After making corrections for impurities, etc., in the gases, Gay-Lussac and Humboldt stated that "100 volumes of oxygen required for complete saturation 199.89 volumes of hydrogen, for which 200 may be put without error." A. Scott (1893) found, as the result of twelve experiments on the volumetric composition of water, that oxygen and hydrogen combine very nearly in the ratio 1 : 2.00245 by volume.

Struck by the simplicity of the relation thus found, J. F. Gay-Lussac (1808) followed up the subject by numerous experiments with different gases. As a result, he concluded that "gases always combine in the simplest proportions by volume." For instance, one volume of hydrogen combines with one volume of chlorine forming two volumes of hydrogen chloride; this fact can be represented diagrammatically:



Two volumes of hydrogen combine with one volume of oxygen forming

two volumes of water vapour (which condenses to liquid water if the temperature be below 100°)

$$\underbrace{\boxed{H}+\boxed{H}+\boxed{O}}_{\textit{3 Volumes.}}=\underbrace{\boxed{H_2O}\boxed{H_2O}}_{\textit{2 Volumes}}$$

Three volumes of hydrogen and one volume of nitrogen form two volumes of ammonia. Thus

$$\underbrace{\boxed{H}+\boxed{H}+\boxed{H}+\boxed{N}}_{\textit{4 Volumes}}=\underbrace{\boxed{NH_3}\boxed{NH_3}}_{\textit{2 Volumes}}$$

There are slight deviations with the gases which show deviations from the laws of Boyle and Charles, but the experimental results are such as to leave no doubt that Gay Lussac's generalization is valid, and accordingly, we define Gay-Lussac's law, when gases react together, they do so in volumes which bear a simple ratio to one another, and to the volume of the gaseous product of the action It is assumed, of course, that the initial and final products of the reaction are under the same conditions of temperature and pressure

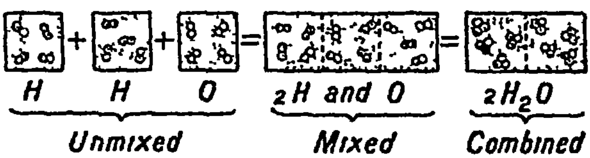
We traced the remarkable way in which elements combine by weight to a peculiarity in the constitution of matter, so here, we are tempted to make a similar quest It follows at once (1) if elements in a gaseous state unite in simple proportions by volume, and (2) if the elements also unite in simple proportions by *atoms*, then the number of atoms in equal volumes of the reacting gases must be simply related With J Dalton let us make a guess. Assume that equal volumes of the different gases under the same physical conditions contain an equal number—say n—of atoms Then, when two volumes of hydrogen react with one volume of oxygen to form two volumes of steam, we have $2n$ atoms of hydrogen reacting with n atoms of oxygen to form $2n$ "compound atoms" of steam Hence, two atoms of hydrogen react with one atom of oxygen to form two "compound atoms" of steam In that case, every atom of oxygen must be split into half an atom to make two "compound atoms" of steam This contradicts the fundamental postulate of the atomic theory—atoms are indivisible in chemical reactions Similar contradictions are encountered in nearly every case of combination between gases, hence Dalton claimed this guess to be untenable, we must try another There is such a marked uniformity in the deportment of elementary and compound gases with respect to variations of temperature and pressure, that it is not very probable any essential difference will be found in the constitution of elementary and compound gases.

§ 2 Avogadro's Hypothesis

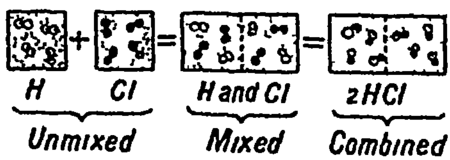
Advances in knowledge are not commonly made without the previous exercise of some boldness and licence in guessing —W WHEWELL.

A Avogadro (1811) pointed out that the fallacy in Gay Lussac's reasoning can be avoided if we distinguish clearly between elementary

atoms and the small particles of a gas Assume that the small particles of a gas are aggregates of a definite number of atoms Avogadro called these aggregates molecules in order to distinguish them from the ultimate atoms The term "molecule" is the diminutive form of the Latin word *moles*, a mass. Each molecule of an elementary gas contains the same number and kind of atoms. For the sake of simplicity, assume that each molecule of hydrogen gas is composed of two atoms of hydrogen, and make a similar assumption for oxygen gas. Hence, modify Gay-Lussac's guess and assume that equal volumes of all gases contain the same number of molecules Suppose that two volumes of hydrogen contain $2n$ molecules of hydrogen, then one volume of oxygen will contain n molecules These react to form $2n$ molecules of steam—each molecule of steam contains two atoms of hydrogen and one atom of oxygen The idea can be more clearly illustrated by means of the subjoined diagrams Each square represents one volume of a gas Each volume contains n molecules We do not know the numerical value of n, but, for the sake of simplicity, take $n = 4$ It makes no difference to the final conclusion what numerical value we assign to n Then we have



Again, with hydrogen and chlorine,



Diagrams similar to these were used by A Gaudin, 1832 It must not be supposed for one moment that these diagrams are intended as pictures of the actual molecules They are to be regarded as aids to the understanding of how Avogadro's hypothesis has led chemists to conclude that the molecules of gaseous elements are really compounded atoms, and how Avogadro's hypothesis reconciles the observed volume relations during the combination of gases with the atomic theory

We have assumed for the sake of simplicity, that the molecule of water contains three atoms, and that each molecule of hydrogen and oxygen contains two atoms As a matter of fact, all we can infer from the observed facts is that the molecule of oxygen is split into halves, and in the absence of evidence to the contrary, we must assume for every substance the simplest molecular structure consistent with the observed facts

Avogadro thus modified the atomic hypothesis and adapted it particularly to gases According to Avogadro, a molecule is the smallest particle of an element or compound which exists free in a gas This definition of a molecule is usually extended into the less satisfactory definition A molecule is the smallest particle of an element or compound which exists in a free state A diatomic molecule for gaseous chlorine, hydrogen, and oxygen at ordinary temperatures, is a satisfactory

explanation of what we know to day, but it is possible that at some future date, the evidence will compel us to consider these molecules to be tetra- or hexatomic. This will not materially affect the principle as indicated above. The molecule of mercury, as we shall see later is supposed to be monatomic, and the molecule of sulphur hexatomic. **Avogadro's hypothesis states that equal volumes of all gases, at the same temperature and pressure, contain the same number of *molecules*.** A M Ampère tried unsuccessfully to extend the same hypothesis to solids in 1814.

Increasing knowledge has made the hypothesis more and more probable, it has been tested in hundreds of experiments, and never found wanting. The hypothesis has done such good service in giving a rational explanation of many different phenomena that it has been accepted as a fundamental truth.[1] Avogadro's hypothesis is the basis of the current theory of chemistry.

§ 3 The Relative Weights of the Molecules

In order to bring into harmony all the branches of chemistry, we must have recourse to the complete application of the theory of Avogadro and Ampère in order to compare the weights and the numbers of the *molecules*.—S CANNIZZARO

Avogadro's hypothesis has proved to be one of the most suggestive and fruitful hypotheses in the development of chemistry. It has correlated what appeared antagonistic and contradictory, it has harmonized what seemed discordant and confused, and made Dalton's atomic hypothesis a clear, intelligible, and fertile theory. Had it not been for this development, Dalton's hypothesis was in a fair way of being "sentenced to sterility and oblivion" (A. Würtz, 1887).

By definition, the relative density of a gas is a number which represents how much heavier any volume of the gas is than an equal volume of the standard gas—generally hydrogen—measured at the same temperature and pressure—generally at 0° and 760 mm pressure. Thus, the relative density of steam is 8.95. This means that any volume, say a litre of steam, is nearly nine times as heavy as the same volume of hydrogen.[2]

By Avogadro's hypothesis, equal volumes of gases contain the same number of molecules, consequently, the relative density of a gas is proportional to its molecular weight. If we accept this deduction, it enables us to determine the molecular weights of gases, once we have fixed an arbitrary standard for the density. Cannizzaro's unit hydrogen = 2, is generally taken as the standard, or as Cannizzaro expressed it, "the quantity of hydrogen contained in a molecule of hydrogen chloride" is taken as unity. **The determination of the molecular weight of a gas is thus reduced to a laboratory measurement—the determination of the relative density of the gas.** Methods for

[1] Deviations from Avogadro's law are observed with those gases which deviate from Boyle's and Charles' laws. With hydrogen the deviation is scarcely noticeable, with chlorine the deviation is about $1\frac{1}{2}$ per cent.

[2] Strictly speaking, the density of a gas is the weight of 1 c.c. of the gas at 0° and 760 mm. The density of a gas is usually expressed in terms of a litre of the gas because the number representing the weight of 1 c.c. would be inconveniently small.

measuring vapour densities are described in a later chapter The numerical values for the molecular weight and the relative density of a gas referred to hydrogen (= 2) are the same [1] That is,

$$\text{Molecular weight} = \text{Relative density } (H_2 = 2) \qquad (1)$$

If the density be determined, as is frequently the case, with reference to air = unity, then, since the density of air with reference to $H_2 = 2$ is 28 75, or with reference to $O_2 = 32$, 28 98, it follows

$$\text{Molecular weight} = 28\ 98 \times \text{Relative density (air} = 1) \qquad (2)$$

These very important deductions were made by S Cannizzaro in a pamphlet published in 1858 Before this step was taken, rank confusion prevailed in chemical literature The terms "atomic weight," "combining weight," and "molecular weight" were used and abused in every conceivable way After reading Cannizzaro's pamphlet, Lothar Meyer (1860) said "the scales fell from my eyes, my doubts disappeared, and a feeling of tranquil security took their place"

Cannizzaro gave the following numbers, among others, for the densities of the different gases referred to hydrogen taken as 2, or to a semi-molecule of hydrogen taken as unity

	Relative densities
Hydrogen	2 0
Ordinary oxygen	32 0
Chlorine	71 0
Nitrogen	28 0
Water vapour	18 0
Hydrogen chloride	36 5

If, therefore, the molecules of hydrogen, oxygen, nitrogen, and chlorine contain two atoms, the atomic weights of these gases will be half the respective molecular weights. Hence

TABLE II —CANNIZZARO'S TABLE OF ATOMIC WEIGHTS

Element	Relative density of gas	Atomic Weight Density ÷ 2
Hydrogen	2	1 0
Oxygen	32	16 0
Chlorine	71	35 5
Nitrogen	28	14 0

In the case of compounds, if the molecule of hydrogen chloride contains an atom of chlorine and an atom of hydrogen, the molecular weight will be $35\ 5 + 1 = 36\ 5$, and the molecule of water vapour containing two atoms of hydrogen and one atom of oxygen, will have a molecular weight of $16 + 2 = 18$ Hence, given the molecular weight of a compound gas, and the weights of the atoms of all but one of the elements, it is possible to compute the weight of the atom or atoms of that element in

[1] The student must be careful to note that if the unit be H = 1 or O = 16, the relative density = ½ *molecular weight*, *or the molecular weight* = 2 × relative density It is unfortunate that these different units are employed even though all give the same final result The questions appended to this and some subsequent chapters have been compiled from different sources, and the different units have not been reduced to one uniform system

the molecule in question. The *modus operandi* will be discussed in the next two sections.

Avogadro explicitly guarded against the assumption that the number of constituent atoms must always be 2. There is really nothing in the facts to justify the assumption that the atoms are simple particles. For all we know to the contrary, the atoms may be clusters of n particles. Indeed, we shall soon review some cogent evidence which has led to the inference that Dalton's atoms are not nature's irreducible minima. Even if this inference be valid, each cluster of n particles has a definite weight—atomic weight—and enters into and is expelled from chemical combination as if it were a simple particle. If an atom be a cluster of particles, each cluster, so far as we can tell, has up to the present time behaved in chemical reactions as if it were an individual particle.

Problem.—*To deduce Avogadro's law from the relation between the relative densities and the molecular weights of the gases.* Let M_1 and M_2 denote the weights of the molecules of two gases—A and B respectively; further let n_1 and n_2 respectively denote the number of molecules in unit volumes of the two gases. The weights of unit volumes (*i.e.* the densities) of the two gases will be M_1n_1 and M_2n_2. The observed fact is that the molecular weights (M_1 and M_2) of the gases are proportional to the densities (M_1n_1 and M_2n_2) of the gases; or $M_1n_1 : M_2n_2 = M_1 : M_2$, from which it follows that in unit volumes of the two gases $n_1 = n_2$. This is the symbolic way of stating Avogadro's law. Hence, it has been claimed that Avogadro's postulate can be deduced from the relation between the molecular weights and the densities of two gases.

This is a convenient example for cautioning the student not to be misled by the apparent precision and rigorous accuracy conveyed to his mind by reasoning expressed in mathematical symbols. Some affirm, on the strength of the simple demonstration just indicated, that "Avogadro's hypothesis is true." The reasoning is perfectly sound, but what about the premises, or statements upon which the reasoning is based? If the student has followed the description of Avogadro's work, he will see that the method for the determination of molecular weights tacitly assumes Avogadro's hypothesis is true. Hence, if the mathematical demonstration be employed to *prove* that "Avogadro's hypothesis is true," we argue in a vicious circle. We have assumed in the premises what we sought to "prove" in the demonstration.

§ 4. The Formulæ of Compounds.

> Avogadro's hypothesis affords a bridge by which we can pass from large volumes of gases which we can handle, to the minuter molecules, which individually are invisible and intangible.—W. A. SHENSTONE.

Since Cannizzaro's time, an enormous number of molecular weights have been determined by the vapour density method. If the molecule cannot be decomposed, we must assume that it is composed of one kind of matter only. If the substance is compound, it must be analyzed so as to find the ratio, by weight, of its component elements referred to the oxygen standard (16). For instance, suppose that the analysis of a gaseous compound furnished

Nitrogen 82.35 per cent.; Hydrogen 17.65 per cent.

Using Cannizzaro's atomic weights, p 59, oxygen = 16, hydrogen = 1, and nitrogen 14, the compound has its nitrogen and hydrogen atoms in the following proportion by weight

$$\frac{82\ 35}{14}\text{ nitrogen atoms}\quad\frac{17\ 65}{1}\text{ hydrogen atoms}$$

That is,

5 9 nitrogen atoms   17 65 hydrogen atoms

By hypothesis we cannot have fractions of atoms The nearest whole numbers are 3 hydrogen atoms for one nitrogen atom Since the sum of the atoms in the compound must represent the molecular weight, it follows that the molecular weight must be $3n + 14n = 17n$ Or the molecular weight is 17×1, 17×2, 17×3, or $17n$ The formula is N_nH_{3n} We can get no further until we know the molecular weight If the vapour density of the compound (hydrogen = 2) be 17, the molecular weight is 17 Hence, $17 = 17n$, or $n = 1$ The compound analysed can therefore be represented by the formula NH_3

EXAMPLES —(1) As indicated on p 47, E W Morley (1895) found, in some careful experiments on the synthesis of water, that hydrogen used 3 7198 grms , oxygen used 29 5335 grms , water formed 33 2530 grms That is, one part by weight of hydrogen combines with 7 94 parts by weight of oxygen to produce 8 94 parts by weight of steam A molecule of steam must contain n atoms of hydrogen, because parts of an atom do not take part in chemical changes Hence n parts by weight of hydrogen per 7 94n parts by weight of oxygen give a molecule of steam of weight 8 94n This all follows from the atomic theory To apply Avogadro's hypothesis, with Cannizzaro's standard, the density of the steam must be determined It lies between 16 and 20 It is difficult to determine the number exactly If $n = 1$, the density of the steam molecule will be near 8 94 This does not agree with the observed density 16 to 20 If $n = 2$, the density of the steam will be 17 88 , and if $n = 3$, the density of steam will be 26 82 Hence, $n = 2$ This means that each molecule of water vapour contains 2 atoms of hydrogen, atomic weight 1, and one atom of oxygen atomic weight 15 88 , or if we make our unit oxygen = 16, the atomic weight of hydrogen will be 1 008

(2) Two different compounds have the same ultimate composition, namely carbon 92 31 per cent , hydrogen 7 69 per cent , but the one has a relative density 26, and the other a relative density 78 (H=2) What is the formula of each compound ? There are $92\ 31 - 12 = 7\ 7$ carbon atoms per $7\ 7 - 1 = 7\ 7$ hydrogen atoms But we cannot have fractions of atoms, hence dividing by 7 7 we get the ratio 1 1 That is, the formula of the compound is C_nH_n The molecular weights of this series of compounds is $(12 + 1)n$ or $13n$ If $n = 2$, the molecular weight will be 26 Hence, one of the compounds is C_2H_2, and the other is C_6H_6

In calculating formulæ for substances which cannot be vaporized, and one of the methods to be described later cannot be applied, it is usual to assume that the molecule has the simplest possible formula In that case the formula is said to be *empirical* Some prefer to use the term "formula weight" in place of "molecular weight" when the actual molecular weight has not been determined The formula weight, like the molecular weight of a compound, is the sum of the atomic weights of the elements represented by the known or assumed formula of the compound

EXAMPLES —(1) 10 grams of pure tin when oxidized in air gave 12 7 grams of oxide What is the formula of tin oxide ? The atomic weight of tin is 119, and of oxygen 16 Hence, the ratio Tin oxygen = 10 ÷ 119 2 7 ÷ 16 = 0 084 0 17 = 1 2 The formula is therefore written SnO_2, although there is nothing to show why it is not Sn_2O_4 , Sn_3O_6 , Sn_nO_{2n}

(2) A sample of crystallized sodium carbonate furnished on analysis 37 2 per

cent of Na_2CO_3, and 62 8 per cent of H_2O What is the formula of the compound? The ratio Na_2CO_3 $H_2O = 37\ 2 - 106\quad 62\ 8 \div 18 = 0\ 35\quad 3\ 49 = 1\quad 10$ Hence, the formula is taken as $Na_2CO_3\ 10H_2O$, although there is nothing to show why it is not some multiple of this, say, $nNa_2CO_3\ 10nH_2O$

§ 5 The Relative Weights of the Atoms

It has already been stated that the conceptions "molecular weight" and "atomic weight" are quite independent of our theories about the nature of atoms and molecules, nor are the conceptions much affected by the actual weights of the atoms and molecules because the terms under consideration are definite expressions of Avogadro's hypothesis coupled with observed facts. It might therefore have been misleading to head this paragraph "Weighing the Atoms" There are reasons for supposing that the molecular weight of some compounds in the liquid or solid condition is a multiple of the molecular weight of the same substance in the gaseous condition The molecule of steam approximately corresponds with the formula H_2O, but in liquid water there are reasons for supposing the molecule is either $(H_2O)_3$ or $(H_2O)_4$, that is, the formula for liquid water is not H_2O, but either H_6O_3 or H_8O_4

Refer back to the difficulty in fixing the atomic weight of carbon from the ratio of the weights of carbon and oxygen in the two oxides of carbon which we encountered in applying Dalton's atomic theory Suppose that we do not know the atomic weight of carbon, but that we do know the composition of a number of volatile carbon compounds as well as their relative densities or molecular weights, Table III.

TABLE III —MOLECULAR WEIGHTS OF SOME CARBON COMPOUNDS

Volatile compound of carbon	Composition by weight	Molecular weight	Amount of carbon per molecule
Carbon monoxide	Carbon 12, oxygen 16	28	12
Carbon dioxide	Carbon 12, oxygen 32	44	12
Methane	Carbon 12, hydrogen 4	16	12
Ethylene	Carbon 24 hydrogen 4	28	$12 \times 2 = 24$
Propylene	Carbon 36, hydrogen 6	42	$12 \times 3 = 36$
Carbon disulphide	Carbon 12, sulphur 64	76	12

The smallest weight of carbon in a molecule of any of its known compounds is 12, and consequently this number is assumed to be the atomic weight of carbon The atomic weights of a great number of the elements have been determined in a similar manner

The actual method used in finding the atomic weight of an element thus involves

(1) An exact analysis of a compound containing the given element, and consequently the compound investigated must be one which lends itself to exact analysis.

(2) The compound must be one which can be prepared in a highly purified condition

(3) The compound must be volatile without decomposition, so that its vapour density can be determined

(4) The compound must contain the smallest proportion of the element under investigation Thus matter may need further amplification.

In 1894, J A Wanklyn claimed to have discovered a series of hydrocarbons, one member of which contained carbon 102 parts by weight, and hydrogen 17 parts, and had a vapour density of nearly 116 (hydrogen 2) Assuming the atomic weight of carbon is 12, and of hydrogen 1, these numbers give formula $C_{8.5}H_{17}$ If this statement had been corroborated, and we were quite sure that Wanklyn's hydrocarbons were not mixtures, it would be necessary to make the atomic weight of carbon = 6, and write the formula of the compound in question $C_{17}H_{17}$, and this in spite of the fact that thousands of compounds of carbon are known, and all agree with the number 12 for the atomic weight of carbon The formula of carbon monoxide—CO—would then be written C_2O, etc. But Wanklyn's claim has never been established

These remarks emphasize the importance of examining as large a number of volatile compounds as possible when fixing the atomic weight of an element If only a small number of compounds be examined, there is always a possibility, and perhaps a probability, that the actual minimum weight does not occur amongst the set of compounds taken It follows, therefore, that the atomic weight of an element is the least amount of that element present in any molecule of all its known volatile compounds. The value so obtained is the maximum possible value, the real value may afterwards prove to be a submultiple of this. The atomic weight must be a whole multiple or submultiple of its combining weight Owing to the fact that the molecular weights of so many volatile compounds of carbon are known, it is not very probable that the atomic weight of carbon is less than 12

There are several other methods of computing molecular and atomic weights of the different elements Fortunately, atoms and molecules possess other qualities besides mass which are dependent upon their "atomic weights" and which can be readily measured Some of these will be described later

§ 6 The Elements

What are the best representative values for the atomic weights of the elements?—The best available determinations of the value of the oxygen-hydrogen ratio give numbers ranging between 1 005 and 1 008 when the standard of reference is oxygen 16 All measurements made by man are affected by unavoidable errors of experiment, and measurements of the numerical value of all constants differ within certain limits amongst themselves (see p 15) It is convenient to select one representative value from the set of different observations ranging between the limits 1 005 and 1 008 The majority of chemists have agreed to let the International Committee of Atomic Weights decide what are the best representative values for the atomic weights of all the elements year by year. Hence, the generally accepted ratio for the atomic weights of hydrogen and oxygen is 1 008 16 Every time new and more refined methods of measurement are employed, a change—generally insignificantly small—may be necessary The student must recognize that the true atomic weights cannot be altered by the votes of the majority of the members on the International Committee of Atomic Weights There is an uncertain factor in the accepted values of the atomic weights, as there is in all our

judgments. Aristotle was no doubt right, "nothing can be positively known and even this cannot be positively asserted." This doctrine, however, if rigorously applied, would paralyze all action. Accordingly, sound minded people are accustomed to balance the evidence and then act. A careful consideration of all the available evidence considerably reduces the risk of error, and this method, adopted by the Committee, appears to be the most satisfactory solution of the problem.

The atomic weights of a few of the more important elements are indicated in the following table. The numbers are those recommended by the International Committee on Atomic Weights. The full table appears inside the front cover of this book.

TABLE IV.—INTERNATIONAL ATOMIC WEIGHTS. O=16

Aluminium	Al	27.1	Iron	Fe	55.84
Antimony	Sb	120.2	Lead	Pb	207.20
Arsenic	As	74.96	Magnesium	Mg	24.32
Barium	Ba	137.37	Manganese	Mn	54.93
Bismuth	Bi	208.0	Mercury	Hg	200.6
Boron	B	11.0	Nickel	Ni	58.68
Bromine	Br	79.92	Nitrogen	N	14.01
Calcium	Ca	40.07	Oxygen	O	16.00
Carbon	C	12.005	Phosphorus	P	31.04
Chlorine	Cl	35.46	Platinum	Pt	195.2
Chromium	Cr	52.0	Potassium	K	39.10
Cobalt	Co	58.97	Silicon	Si	28.3
Copper	Cu	63.57	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gold	Au	197.2	Sulphur	S	32.06
Hydrogen	H	1.008	Tin	Sn	118.7
Iodine	I	126.92	Zinc	Zn	65.37

For ordinary calculations involving the use of atomic weights, all the atomic weights, excepting chlorine (35.5), copper (63.5), nickel (58.5), and zinc (65.5), are rounded off to the nearest whole numbers. The elements just named are then assigned the atomic weights indicated in the brackets. Some chemists—G. D. Hinrichs, for example—firmly believe that the rounded numbers are the best representative values of the atomic weights, and that the small deviations from the rounded numbers indicated in the "International Table" represent real, if unrecognized errors of experiment.

Why is oxygen = 16 taken as the standard?—During the latter part of the nineteenth century, J. Dalton's (1803) standard, hydrogen = 1, was used for the atomic weights instead of oxygen = 16. Hydrogen was selected because it is the lightest element known. J. S. Stas (1860–65) pointed out that the determination of the atomic weight of an element should be connected with the standard as directly as possible. Very few compounds of the metals with hydrogen are suitable for an atomic weight determination, while nearly *all* the elements form stable compounds with oxygen. Hence, if hydrogen be the standard, it is necessary to find the exact relation between the given element and oxygen, and then calculate what that relation would be on the assumption that the relation between hydrogen and oxygen is known. Every improved determination of the relation between hydrogen and oxygen would then be followed by an alteration in the atomic weight of every other element whose value,

with respect to hydrogen as a standard, has been determined by the indirect process just indicated The determination of the exact relation between hydrogen and oxygen appears to be more difficult than many other determinations and hence, the majority of chemists think it better to refer the atomic weights of the elements to oxygen = 16 as the standard instead of making the atomic weights depend on the more or less uncertain relation H O The standard oxygen = 16 is quite arbitrary T Thomson (1825) used oxygen = 1, W H Wollaston (1814), 10, J S Stas (1860–65), 16; and J J Berzelius (1830) used oxygen = 100 as standard The latter number makes the atomic weights of many elements inconveniently large, and if the atomic weight of oxygen be any whole number less than 16, fractional atomic weights will be required The use of the "oxygen-16" unit involves the least change in the numbers which were in vogue when "hydrogen-unity" was the standard

Division of the elements into metals and non-metals—It is often convenient to divide the elements into two groups metals and non-metals Like most systems of classification an exact subdivision is not possible because some elements exhibit properties characteristic of both classes. Very roughly, the properties of the metals can be contrasted against the properties of the non-metals as indicated in the subjoined scheme

TABLE V—THE PROPERTIES OF THE METALS AND NON-METALS CONTRASTED

Metals	Non-metals
1 Form basic oxides	1 Form acidic oxides
2 Generally dissolve in mineral acids giving off hydrogen	2 Do not usually dissolve easily in mineral acids
3 Either form no compounds with hydrogen, or form unstable compounds—usually non volatile	3 Form stable compounds with hydrogen—these are usually volatile
4 Solid at ordinary temperature (excepting mercury)	4 Gases, liquids or solids at ordinary temperatures
5 Usually volatilize only at high temperatures	5 Excepting carbon boron, and silicon, the non metals are either gaseous or volatilize at low temperatures
6 When in bulk the metals reflect light from polished or freshly cut surfaces	6 Do not usually reflect light very well
7 Specific gravity is generally high	7 Specific gravity generally low
8 Good conductors of heat and electricity	8 Bad conductors of heat and electricity
9 More or less malleable and ductile	9 Malleability and ductility are not well defined

To show how difficult it is to draw a hard-and-fast line of demarcation between metals and non-metals, the non-metals arsenic, antimony, and tellurium would be classed with the metals if we depended exclusively upon 6, 7, and 8, hence, some introduce a third division—the metalloids—to include the hybrids, or elements which have properties characteristic of both the metals and the non-metals The metals lithium, sodium, potassium, magnesium, and aluminium have a low specific gravity The non-metals carbon, boron, and silicon are less volatile than most metals The non metal hydrogen is a good conductor of heat; and the non-metal

graphitic carbon is a good conductor of heat and electricity Hence the division of the elements into metal and non metals is but a rough system of classification, arbitrarily adopted because it is convenient.

In all systems of classification, the attempt is made to bring together in one group the things which are alike in general properties, and to separate those which are unlike The attempt to group the elements by a code of definitions is foredoomed to failure. There is a seductive simplicity about a definition which may be attractive, but it is artificial and often misleading As T Campanella (1590) expressed it "Definition is the end and epilogue of science It is not the beginning of our knowing, but only of our teaching"

§ 7 The Relation between the Molecular Weights and the Volumes of Gases

The molecular weight of any gas is numerically equal to the weight of any volume of the gas when the weight of an equal volume of hydrogen under the same physical conditions of temperature and pressure is 2 Two grams of hydrogen, taken as the standard, occupy 22 4 litres at normal temperature—0°—and normal pressure—760 mm of mercury Hence, it follows directly from Avogadro's hypothesis that the molecular weight of any gas, expressed in grams, occupies, approximately, 22 3 litres at 0° and 760 mm pressure Consequently, to find the molecular weight of a gaseous substance, weigh 22 3 litres of the gas at a convenient temperature and pressure, calculate the corresponding volume at 0° and 760 mm pressure, and calculate by proportion the weight of 22 3 litres.

EXAMPLE —A litre of gas at 20° and 730 mm weighs 1 764 grams, what is the molecular weight of the gas? By the method of calculation indicated in the next chapter, one litre of a gas at 20° and 730 mm pressure contracts to 894 5 c c at 760 mm and 0° Hence, if 894 5 c c weigh 1 764 grams, 22 3 litres will weigh 43 97 grams Hence the molecular weight of the gas is nearly 44

It must here be mentioned that the number 22 3 is not quite right for all gases Many gaseous molecules have a slight attraction for one another, so that the molecules are slightly more closely packed than is represented by Avogadro's hypothesis The greater the intermolecular attraction, the greater the weight of 22 3 litres, and consequently, the less the volume of a molecular weight of the gas expressed in grams Thus, experiment shows

Hydrogen	Oxygen	Nitrogen	Chlorine	Hydrogen chloride	Carbon dioxide	Steam (0°,760 mm)	Mercury
22 40	22 39	22 45	22 01	22 22	22 26	22 39	22 55

The deviation from 22 3 can be neglected in ordinary chemical calculations

The molecular weight of a compound not only tells us a weight, but it also tells us that if the molecular weight be expressed in grams, the gas will occupy 22 3 litres at 0° and 760 mm Further, the molecular weight of a gas, expressed in kilograms, occupies, approximately, 22 3 cubic metres at 0° and 760 mm pressure By mere chance, the number of avoirdupois ounces in a kilogram is 35 26, which is very nearly the same as the number of cubic feet in a cubic metre (35 31)—J W Richards. The difference is only one seventh of one per cent. Hence, the molecular

weight of any gas, expressed in avoirdupois ounces, occupies, approximately 22.3 cubic feet at 0° and 760 mm pressure These factors are useful in calculations involving cubic feet, cubic metres, and litres

§ 8 Chemical Equations

When the initial and final products of a chemical reaction as well as the composition and proportions of the molecules concerned in the reaction are known, the facts can usually be symbolized in the form of a chemical equation There are some limitations which will be described later

1 The equation indicates the nature of the atoms and the supposed composition of the molecules concerned in the reaction; as well as the proportions of the different molecules in the initial and final products of the reaction —For instance when mercury is heated in air, and mercuric oxide, HgO is formed, the reaction can be represented in symbols: $2Hg + O_2 = 2HgO$ We here ignore the nitrogen of the air because, so far as we can tell it plays no direct part in the chemical reaction. Similarly, when mercuric oxide is heated to a high temperature it decomposes, forming metallic mercury and oxygen In symbols, $2HgO = 2Hg + O_2$. The symbol "$=$" is used instead of the words "produces" or "forms," and the symbol "$+$" is used for "together with" on the right side of the "$=$" sign, and for "reacts with" on the left side The latter equation reads: "Two molecules of mercuric oxide, on decomposing, produce a molecule of oxygen and two molecules of monatomic mercury" The number and kind of the atoms of the two sides of the equation must always be the same (persistence of weight)

2 The equation indicates the proportions by weight of the substances concerned in the reaction —The atomic weight of mercury is 200, and the atomic weight of oxygen is 16, hence, the molecular weight of mercuric oxide is 216, and of oxygen 32 The latter equation can therefore be read: "432 grams (ozs or tons) of mercuric oxide in decomposing, form 32 grams (ozs or tons) of oxygen gas and 400 grams (ozs or tons) of metallic mercury Hence the chemical equation can be employed in all kinds of arithmetical problems dealing with weights of substances formed or produced.

EXAMPLES —(1) How much mercuric oxide is required to furnish 20 grams of oxygen gas? Write down the proper equation, write 432 below the mercuric oxide, and 32 below the oxygen We are not concerned with the mercury in this problem Since we read, from the equation 32 grams of oxygen are furnished by 432 grams of mercuric oxide, one gram of oxygen will be furnished by $432 \div 32 =$ 13.5 grams of mercuric oxide, and 20 grams of oxygen will come from $20 \times 13.5 =$ 270 grams of mercuric oxide

(2) How much oxygen can be obtained from 30 grams of mercuric oxide? Answer $2\frac{2}{9}$ grams

3 The equation indicates the proportions by volume of the gases concerned in the reaction —We have seen in the preceding section that if we express

Molecular weights in	Volume at 0° and 760 mm per molecular weight
Grams	22.3 litres
Kilograms	22.3 cubic metres.
Ozs (avoir)	22.3 cubic feet.

Consequently, we can express the idea conveyed by the equation, $2HgO = O_2 + 2Hg$ in these words "432 grams (kilograms or ozs) of

mercuric oxide will furnish 32 grams (kilograms or ozs) of oxygen, or 22 3 litres (cub metres or cub ft) of oxygen gas at 0° and 760 mm, and 400 grams of mercury "

EXAMPLES —(1) What volume of oxygen will be obtained by heating 30 grams of mercuric oxide? 432 grams of mercuric oxide will furnish 22 3 litres of oxygen gas, hence 30 grams will furnish $30 \times 22\ 3 \div 432 = 1\ 55$ litres of oxygen gas at 0° and 760 mm pressure

(2) How much mercuric oxide will be needed for 10 cub ft of oxygen gas at 0° and 760 mm pressure? Here 22 3 cub ft of the gas come from 432 ozs of mercuric oxide, hence, $432 \times 10 \div 22\ 3 = 193$ ozs, or 12 lbs 1 oz of mercuric oxide are required

§ 9 The Relation between Atomic and Combining Weights—Valency

When the *formulæ* of inorganic compounds are examined even a superficial observer is struck by their general symmetry Without offering any hypothesis as to the cause of this symmetrical grouping of the atoms, it is sufficiently evident that such a tendency exists, and that the combining power of the atoms of the attracting elements is always satisfied by the same number of atoms without reference to the chemical behaviour of the uniting atoms —E FRANKLAND

Observation shows that the relative combining weights of oxygen and hydrogen are very nearly as O H = 8 1, and that the atomic weights of oxygen and hydrogen, deduced from the atomic theory and Avogadro's hypothesis, are very nearly as O H = 16 1 In fine, the atomic weight of oxygen is twice its combining weight For carbon in carbon dioxide, we have the combining weight 3, while the atomic weight of carbon is 12, that is, the atomic weight of carbon is four times the combining weight In the case of hydrogen and chlorine, the atomic and combining weights are the same The number of times the combining weight or equivalent is contained in the atomic weight is called the valency of the element Hence,

$$\frac{\text{Atomic weight}}{\text{Combining weight}} = \text{Valency}$$

This means that when the combining or equivalent weight of an element is multiplied by an integer representing the valency of the element, the product is the atomic weight

The meaning of valency can be represented another way, for valency also represents a "habit" of an element for combination, it has nothing to do with the force holding the atoms together The valency of an element is obtained by finding—directly or indirectly—how many atoms of hydrogen can combine with or be replaced by an atom of the given element. The valency of hydrogen is always taken as unity Hence the definition 'The valency of an element is a number which expresses how many atoms of hydrogen, or of other atoms equivalent to hydrogen, can unite with one atom of the element in question'

Nomenclature—With hydrogen and chlorine the atomic and combining weights are the same, and the valency is unity These elements are accordingly said to be univalent, or monads, for similar reasons oxygen is bivalent, or a dyad, nitrogen is tervalent, or a triad, and carbon is quadrivalent, or a tetrad

The valency of an element is frequently represented by attaching the necessary number, in dashes or Roman numerals, to the top right hand

corner of the symbol for the element, as suggested by W Odling in 1855 Thus, the symbols H^{I} and Cl^{I} respectively mean that hydrogen and chlorine are univalent, O^{II} means that oxygen is bivalent, N^{III} means that nitrogen is tervalent, and C^{IV} that carbon is quadrivalent By collecting together a few compounds with their symbols, the idea can be made clearer

Univalent	Bivalent	Tervalent	Quadrivalent	Quinquevalent	Sexivalent
$H^{I}Cl^{I}$	$H_2^{I}O^{II}$	$H_3^{I}N^{III}$	$H_4^{I}C^{IV}$	$P^{V}F_5^{I}$	$S^{VI}F_6^{I}$
$Na^{I}Cl^{I}$	$Mo^{II}Cl_2^{I}$	$Fe^{III}Cl_3^{I}$	$C^{IV}O_2^{II}$	$W^{V}Br_5^{I}$	$U^{VI}F_6^{I}$
$K^{I}I^{I}$	$Zn^{II}Cl_2^{I}$	$Mo^{III}Cl_3^{I}$	$Mo^{IV}Cl_4$	$Mo^{V}Cl_5^{I}$	$Mo^{VI}F_6^{I}$

Some heptads and octads are known The elements generally combine in such a way that an equal number of valencies are opposed to one another.

Structural, graphic, or constitutional formulæ —The valency of an element is sometimes represented by attaching the necessary number of hyphens to the symbol for the element This enables the molecules of a substance to be represented by a kind of graphic formula The symbol for hydrogen will have one hyphen, oxygen, two, nitrogen, three, carbon, four, etc The symbol for hydrogen chloride then becomes H—Cl, potassium iodide, K—I, water, H—O—H, mercuric oxide, Hg=O, a molecule of hydrogen, H—H, a molecule of oxygen, O=O carbon dioxide, O=C=O, and

$$\mathrm{H{-}N}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown \mathrm{H}\end{smallmatrix} \qquad \mathrm{O}\begin{smallmatrix}\diagup \mathrm{Fe{=}O}\\ \diagdown \mathrm{Fe{=}O}\end{smallmatrix} \qquad \begin{smallmatrix}\mathrm{H}\diagdown\\ \mathrm{H}\diagup\end{smallmatrix}\mathrm{C}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown \mathrm{H}\end{smallmatrix}$$

Ammonia Ferric oxide Methane

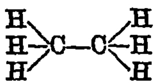
Accordingly, the terms "bonds" or "links" are sometimes employed instead of "valencies" [1]

Graphic formulæ are also called structural or constitutional formulæ *Structural formulæ primarily assume that the chemical properties of a substance are determined by the arrangement of the atoms in the molecules, and if the molecules of two compounds of the same chemical composition have their atoms differently arranged, the properties of the two compounds will be different* Graphic formulæ are sometimes very convenient for representing the composition of compounds, but the student would err rather seriously if he supposes that the symbol given above for, say, methane represents the way the atoms are actually grouped in the molecule of methane This would involve a leap far beyond our real knowledge In some cases, however, the little knowledge we do possess can be better summarized by a graphic formula than in any other way, and the graphic formula furnishes a clearer mental image of the curious way certain groups of atoms remain clustered together through a complex series of chemical changes than if the reaction were represented by ordinary symbols A graphic formula is thus a kind of "dummy" model to illustrate the way a compound is formed, how it decomposes, and the relations between one compound and another The student must not believe for one moment that the model simulates reality The remarkable work which has been done by the aid

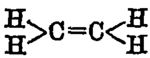
[1] The hyphens are generally attached so that the graphic formula occupies as little space as possible I believe A S Couper first used linking bars between the symbols of the combining elements in 1858, and the present system developed in its present form through the work of A Kekule (1859), C Brown (1866), and E Frankland (1866)

of structural formulæ will always justify their use in the past and present, whatever future generations may think of them.[1]

Maximum and active valency.—Most elements have more than one valency. Stannous oxide has a composition corresponding with SnO, and stannic oxide, SnO_2. In the former case the tin is said to be bivalent, and in the latter, quadrivalent. There are thus two series of tin compounds—stannous and stannic. Similarly with copper, iron, etc. There are also two carbon oxides, carbon monoxide, CO, and carbon dioxide, CO_2. If carbon monoxide could be written $O{=}C{=}C{=}O$, and there is nothing in the analysis by weight which prevents this, all might be well, but writing the formula in this manner would involve a contradiction of Avogadro's hypothesis, since the vapour density of carbon monoxide corresponds with the molecule CO, not C_2O_2. We cannot see the way clear to admit carbon monoxide as an exception to Avogadro's hypothesis, for that would introduce confusion into our system, and there would be no immediate prospect of restoring order. Some get over the difficulty by assuming that two of the free valencies in carbon monoxide mutually saturate one another, and write the graphic formula $O{=}C{<}|$, others assume that oxygen is quadrivalent, and write $C{\equiv}O$. The case of sulphur bivalent in hydrogen sulphide, $H{-}S{-}H$, quadrivalent in sulphur dioxide $O{=}S{=}O$, and sexivalent in sulphur trioxide $\genfrac{}{}{0pt}{}{O}{O}{\gg}S{=}O$, fits very well into this scheme. So do the series of compounds represented by ethane, C_2H_6, ethylene, C_2H_4, and acetylene, C_2H_2, which are respectively represented by the graphic formulæ



Ethane



Ethylene

$H{-}C{\equiv}C{-}H$

Acetylene

It has been supposed that valency is a "fundamental property of the atom which is just as constant and invariable as the atomic weight"—A. Kekulé, and further that each element has a maximum valency towards certain other elements. When an element in a compound appears to have a lower valency than its maximum valency, the compound is said to be an unsaturated compound, in contrast with a saturated compound in which the atoms are exercising their maximum valency. In many unsaturated compounds, the valencies appear to diminish in pairs. The pairs of "sleeping valencies" or "latent bonds" are supposed to be self saturated. As a matter of fact, the hypothesis of the self-saturation

[1] The student will find valency to be a useful aid in remembering the composition of compounds of different elements. Given the valency of 12 elements, each of which can form one compound with 12 other elements of known valency, it is possible to write down the formulæ of 144 compounds which would be very probably in harmony with the known laws of chemical combination. It would be said that $MgCl$ is not a probable compound of magnesium and chlorine, nor is $MgCl_3$, the correct way of writing the combination is $MgCl_2$. The student should therefore remember the valency of each element he studies, and in that way, much that appears confused and disorderly will seem methodical and regular. The valency of an element may be recalled by reference to its compounds with other elements of known valency. Thus, the chemist does not memorize valencies themselves, but recovers them when needed by recalling a familiar compound or compounds. If the valency of magnesium were forgotten and magnesium chloride, $MgCl_2$, were remembered, then, if chlorine be univalent, magnesium is bivalent.

of the bonds in pairs breaks down completely The idea probably arose from the application of an inaccurate hypothesis which is stated in some of the older books on chemistry in words like these "All chemical evidence shows that a body with unsatisfied bonds cannot exist by itself." All chemical evidence, as we shall see, shows nothing of the kind Mercury and many other elements, when vaporized, give gases with one atom molecules

The principle of self-saturation breaks down when applied to the nitrogen oxides say $N^{'''}O^{''}$. The relative density of the gas (Avogadro's hypothesis) will not let us write N_2O_2, that is, $O{=}N{-}N{=}O$ We are therefore confronted with what appears to be an odd unsaturated valency in the molecule $-N{=}O$ Again, molybdenum forms a series of compounds with univalent chlorine or fluorine—$MoCl_2$, $MoCl_3$, $MoCl_4$, $MoCl_5$, and MoF_6, and vanadium forms VCl_2, VCl_3, VCl_4, and VCl_5. In view of facts like these, it is difficult to maintain the thesis that the apparent inconstancy of the valency of an element is due to the mutual "saturation" of pairs of valencies Either a molecule can exist with free valencies, or Kekulé's maximum valency hypothesis breaks down when confronted with facts.

A great many ingenious hypotheses, more or less satisfactory, have been suggested to explain the difficulties. At present we are compelled to frankly admit with W Lossen (1880) and A Claus (1881) that the active valency of an element is a variable habit of combination An explanation of the meaning of valency is thus left open To distinguish between the greatest valency an element is known to exhibit, and the valency which actually prevails in a particular compound, the terms maximum valency and active valency may be respectively employed So far as we can see, the active valency of an element is dependent upon the properties of the atoms of the other elements with which it is combined, as well as on the prevailing physical and chemical conditions to which the element is exposed Indeed, active valency has been compared with friction in so far as it appears to be called into play by external causes which may vary from zero upwards.

Effect of external conditions on the valency of an element—We have just stated that the valency of an element is determined by the physical and chemical conditions under which the element is placed For instance, valency generally diminishes with rise of temperature, *e g*, sulphur trioxide, SO_3, when heated dissociates into sulphur dioxide, SO_2, and oxygen, and carbon dioxide, CO_2, into carbon monoxide, CO, and oxygen Changes in the valency of an element are often induced by oxidizing or reducing agents Thus, ferrous chloride, $FeCl_2$, is oxidized to ferric chloride, $FeCl_3$, by the action of hypochlorous acid, HClO

$$2Fe^{''}Cl_2 + HCl + HClO = 2Fe^{'''}Cl_3 + H_2O$$

and ferric chloride is reduced to ferrous chloride by the action of sulphur dioxide

$$2Fe^{'''}Cl_3 + SO_2 + H_2O = 2Fe^{''}Cl_2 + 2HCl + SO_3$$

At the same time, it will be noticed, the sulphur dioxide is oxidized to sulphur trioxide, $S^{IV}O_2 + O = S^{VI}O_3$ Hence, oxidation usually involves an increase in the valency of an element, and reduction a decrease

History.—In the early days of the atomic theory, atoms were all supposed to have an equal capacity for combination with one another. With the growth of the idea of multiple proportions, and the custom of referring the constitution of compounds to certain types—HCl, H_2O, H_3N, H_4C—supposed to be fundamental, the idea of valency gradually became clear, and it was specially emphasized by E. Frankland in 1851.

Various terms were used for "valency" during the clarification of the concept—e.g., "saturation capacity," "combining capacity," "affinity units," "affinity of degree," "basicity," "atomicity," etc.[1] A. W. Hofmann employed the term "quantivalency" in 1865, and this was shortened to "valency" by H. Wichelhaus, in 1868. The term "valency" (or "valence") is now in general use.

§ 10 Radicals or Radicles

In 1815, J. L. Gay Lussac, after studying the properties of hydrocyanic acid, reported cyanogen, CN, to be "a remarkable example, and at present, a unique example, of a body which, although a compound, plays the part of a single body in its combinations with hydrogen and the metals." Since then, a great number of similar groups have been found. For convenience, they are commonly called "radicals," or, following the custom of the London Chemical Society, "radicles." The word "radical" was previously employed by G. de Morveau and by A. L. Lavoisier with a different meaning. The definition: *a radicle is a group of atoms which can enter into and be expelled from combination without itself undergoing decomposition*, is virtually that given by J. von Liebig in 1838. Each radicle has its own valency; each acts as an unchanging constant in a series of compounds; and each can be replaced by an element, or elements, of like or equivalent valency. A few examples of radicles of different valency may be quoted: Monad radicles—OH, CN (generally written "Cy"), NO_3, NH_4 (sometimes written "Am"), CH_3, etc. Dyad radicles—SO_4, SO_3, CO_3, SiO_3, etc. Triad radicles—PO_4, $Fe^{III}Cy_6$, etc. Tetrad radicles—$Fe^{II}Cy_6$, SiO_4, etc. In very few cases has it been possible to isolate the radicle, but the definition has nothing to say about the independent existence of radicles. "Radicles," said A. Kekulé (1858), "are not firmly closed atomic groups, but they are merely aggregates of atoms placed near together which do not separate in certain reactions, but fall apart in other reactions." For convenience, the term radicle is sometimes applied to an atom in a compound which can be replaced by another atom or radicle without a further change in the nature of the compound; in that case, the radicle is said to be a "simple radicle" in contrast with "compound radicles" which are "groups of atoms."

Questions

For drilling students in the arithmetic of chemistry, it is best to use a special book, e.g. S. Lupton, "Chemical Arithmetic," London, 1892; R. L. Whiteley, "Chemical Calculations," London, 1892; J. Waddell, "The Arithmetic of Chemistry," New York, 1899; C. Baskerville and W. L. Eastabrooke, "Progressive Problems in General Chemistry," New York, 1910; C. J. Woodward,

[1] The term "atomicity" is best reserved to express the number of atoms in the molecule of an element; and "basicity" for the number of stages in which the replaceable hydrogen of an acid can be substituted by a metal.

"Arithmetical Chemistry," London 1895, etc. A number of arithmetical problems are scattered among the questions appended to subsequent chapters of this book.

1. Describe experiments which illustrate the law of combination of gases by volume. It was at one time thought that this law was accounted for by assuming that "equal volumes of all gases at the same temperature and pressure contain the same number of atoms." What facts show that this assumption is incorrect? What hypothesis is now accepted?—*Univ. North Wales.*

2. State some of the facts relating to the union of gases by volume. State the law of combining volumes. Who discovered the law? What hypothesis was propounded to account for the facts underlying the law? What important conclusion follows from this hypothesis?—*Princeton Univ., U.S.A.*

3. It is usually stated that the valency of an element, when variable, differs by two units. Thus the valency of carbon is expressed by the numbers 2 and 4, and of phosphorus 3 and 5. Mention any exceptions to this law and discuss their bearing on the hypothesis that the valency of a body is a fixed and definite quantity.—*London Univ.*

4. A tube contains 45 c.c. of hydrogen and 20.25 c.c. of oxygen, at a temperature of 120° C. In what respects do the contents differ from steam at the same temperature? What effects would be observed on passing a spark through the mixture?—*Cambridge Senior Locals.*

5. Formerly the atomic weight of oxygen was reckoned as 100. With this standard calculate the atomic weight of hydrogen.—*Coll. of Preceptors.*

6. Discuss the question whether H = 1 or O = 16 should be used as the standard for the atomic weights.—*Board of Educ.*

7. Which of the following gases are lighter, and which are heavier than air: O_2, CO, CH_4, NH_3, SO_2, H_2S? Calculate the weight of 10 litres of CO_2 at N.T.P.—*Board of Educ.*

8. Show that the symbol H_2O best represents the formula for water quite independent of the atomic theory. Hints. The combining weights of hydrogen and oxygen in water are as 1 : 8, or 2 : 16, etc. The formula weight of a gas is the weight in grams of 22.3 litres of the gas at standard temperature and pressure. This gives a value approaching 18 as the formula weight of water. Experiment also gives 32 as the formula weight of oxygen, O_2, when the formula weight of hydrogen H_2 = 2 is taken as the standard of reference. The formula weight of a compound is the sum of the symbol weights of the elements in the formula of the compound. The combining volumes of hydrogen and oxygen are as 2 : 1. The only possible formula for water consistent with these conditions is H_2O. If the formula were HO, the equivalent formula weight would be 17; if H_3O, 19; if H_4O, 20; if HO_2, 33, etc.

CHAPTER V

The Physical Properties of Gases

§ 1 The Atmosphere.

The atmosphere in which we live and breathe is really a part of the globe on which we stand. We are not surrounded by mere empty space. On the contrary, we live and move at the bottom of a vast ocean of air, which is just as material as the water which surrounds the flat fish living at the bottom of the sea.

The terms "atmosphere" and "air" are synonymous and interchangeable, but the word "air" is often used when reference is made to a limited portion of the atmosphere. The word "air" was formerly used in the same general sense that the word "gas" is to day. Later the meaning of the word "air" was narrowed to "the atmosphere." The word "atmosphere" is derived from the Greek ἀτμός (atmos) vapour, σφαῖρα (sphaira), the sphere. The term "atmosphere" is also applied to the gaseous envelope or medium surrounding any body whatever be the nature of the gas—air oxygen carbon dioxide, etc. Hence the term "atmospheric air" is often used to emphasize the fact that "air" is the enveloping medium.

The weight of air.—The physical properties of air were studied long before its chemical properties. Aristotle (B.C. 384), in spite of his confused ideas on the nature of gases, considered air to be a material substance which possessed weight; and Hero of Alexandria (B.C. 117) described some experiments to prove that air is a material substance. For instance he said: "If we invert the open end of a vessel, having but one opening, in water, the water does not enter; if a hole be now bored in the upper part of the vessel, water rushes in, and air escapes, as may be felt, for if we place our hand over the orifice, we perceive a rush of wind which is moving air." Gallileo Galilei, in 1632, first demonstrated satisfactorily that air possesses weight, and he also made a rough determination of the specific gravity of air by comparing the relative weights of equal volumes of air and water. Refined experiments show that 1.000 c.c. of dry air weigh 1.293 grms. under standard conditions—760 mm. pressure 0°, and at sea level in latitude 45°. Hence, the specific gravity of air is 0.001293 if water be unity. The specific gravity of air, referred to the standard hydrogen = 2, is 28.75; or with oxygen = 32 as the standard, 28.95.

The death of the hypothesis: "Nature abhors a vacuum."—When a glass cylinder, closed at one end, is filled with water, then closed at the open end with the hand turned upside down, and the hand removed while the open end of the cylinder is under water, the water remains in the cylinder. Throughout the Middle Ages, this experiment was explained by the hypothesis "Nature abhors a vacuum." The rise of water in

pump barrels was explained by the same hypothesis When it was found that water could not be pumped higher than about 34 ft, it followed that the hypothesis required modification, for Nature's horror of a vacuum obviously could only extend to the equivalent of 34 ft. of water.

In 1644, E Torricelli published an account of an experiment which puzzled the philosophers of the time A glass tube—about four feet long, and closed at one end—was filled with mercury, the open end was closed with the thumb, and the tube inverted so that when the thumb was removed, the open end was immersed in mercury, Fig 21 No air was allowed to enter the tube during the operation Instead of the mercury remaining suspended in the tube, as would have been the case with water, the column of mercury fell to such an extent that its height above the surface of the mercury in the dish was nearly 30 inches, or 760 mm Here again, Nature's horror of the vacuum at the top of the tube only extended to the equivalent of 30 inches of mercury. Torricelli abandoned that hypothesis, and concluded, rightly enough, that *the column of mercury was maintained by the air pressing on the surface of the mercury in the outer vessel* B Pascal argued that since mercury is nearly 13½ times as heavy as water, 30 inches of mercury will be equivalent to 34 ft of water, and he accordingly repeated Torricelli's experiment with a tube 46 ft long using water instead of mercury. He obtained a column of water 34 ft long When the experiment was repeated with other liquids, he found, in every case, that the height of the column was inversely as the density of the liquid Hence, it was inferred that the height of the column of mercury is a measure of the pressure of the atmosphere R. Boyle (1665) applied the term *barometer* to Torricelli's instrument—from the Greek *βάρος* (baros), weight, and *μέτρον* (metron), a measure

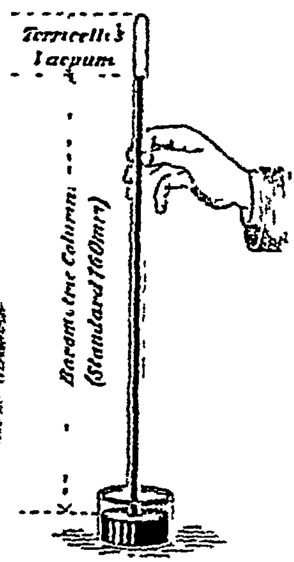


Fig 21 —Torricelli's Experiment

In 1647, B Pascal persuaded M Perier to repeat Torricelli's experiment at the bottom and at the summit of the mountain Puy-de-Dome It was found that the mercury sank lower in the tube the higher up the mountain the tube was carried This proved that the air presses on the bottom of the mountain more than on the top, and not, as Aristotle and his followers would teach, that Nature has a greater horror of a vacuum at sea level than at higher altitudes In a posthumous work, published in 1663, Pascal proved conclusively that *all those effects, previously attributed to Nature's horror of a vacuum are really produced by the pressure, that is, by the weight of the air.* Thus perished the hypothesis "Nature abhors a vacuum"

The pressure and weight of the air—The pressure of the air in any given locality varies within comparatively narrow limits The normal or standard pressure of the atmosphere is equal to the weight of a column of mercury of unit area, and 760 mm high This pressure is sometimes called "one atmosphere" It is merely necessary to know the height of the barometric column to know the weight or pressure of the

air per unit sectional area. This corresponds with a weight of 1033.3 grms. per square centimetre, or 14.7 lbs. per square inch. The word "pressure" is generally used in preference to "weight" because air, like all other fluids, not only presses downwards, but also equally in all other directions.

The extent of the atmosphere.—The air gets less and less dense at higher and higher altitudes, and I. Newton (1706) estimated air to be four times rarer at an elevation of about 7½ miles than at sea level, 1,000,000 times rarer at a height of 76 miles, and 1,000,000,000,000,000,000 times rarer at an altitude of 228 miles, "and so on." It is therefore impossible to place a limit to the height the atmosphere extends.[1] At a height of 100 to 125 miles, there is sufficient air to offer enough resistance to the passage of meteorites to raise their temperature to incandescence. Whatever be the height, the weight of the normal barometric column (per square centimetre of mercury) measures the normal weight of a column of air of the same sectional area and extending from sea level upwards. B. Pascal (1663) appears to have been the first to calculate the total weight of all the air about the globe. His estimate is approximately equivalent to 4,000,000,000,000,000 tons.

§ 2 The Influence of Pressure on the Volume of Gases—Boyle's Law

The quantity of matter in a given body is generally determined by weight, but it is often convenient, when the given body is a gas or liquid, to measure the quantity of matter indirectly by volume. Volumetric analysis is based on such measurements, and the analysis of gases is nearly always conducted by volume measurements. The main advantage of measurement by volume is rapid execution; the main advantage of measurement by weight arises from the fact that the result is largely independent of the physical and chemical conditions of the body in question. The weight of a gas is usually so small in comparison with its volume that it is generally possible to determine the quantity of gas more accurately by volume than by weight.

The volume of a gas is very sensitive to changes of pressure. While investigating the relation between the pressure p and the volume v of a gas, Robert Boyle (1661) found "the pressures and expansions," as he expressed it, "to be in reciprocal proportions." In other words, *the volume of a gas kept at one uniform temperature varies inversely as the pressure.* This is **Boyle's Law**. E. Mariotte, fourteen years after Boyle's publication, reproduced many of Boyle's results as his own; and, on the Continent, the law is sometimes improperly ascribed to Mariotte.

Pressures greater than atmospheric.—The law can be tested in a bent U tube of uniform bore—Fig. 22—similar to that used by Boyle himself.[2] The shorter leg is hermetically sealed at one end, the end of the longer

[1] G. Johnstone Stoney's memoir "The Atmosphere of Planets and Satellites" (1897), does not arrive at any definite limit for our atmosphere, nor for the atmosphere of any other planet, but shows that because the molecules of some gases attain certain high velocities, these gases are able to escape from the atmospheres of the earth and the other planets (see p. 155).

[2] A great many modified forms of this apparatus have been devised for testing the law. These are intended for quick work in student's "first year" laboratories or for the lecture table.

leg is open The tube can be graduated by fixing bits of gummed paper at definite distances Mercury is poured into the longer leg so as to fill the bend and reach to the same height in both legs It may be necessary to tilt the apparatus a little to expel a few bubbles of air from the shorter leg Read the volume of gas confined in the shorter leg Since the level of the mercury is the same in both limbs, it is assumed that the pressure on the surface of the mercury on both sides of the U-tube is the same There is a pressure of one atmosphere on the mercury in the open leg, hence also there is an equivalent pressure of one atmosphere in the mercury in the closed leg A pressure of one atmosphere is equivalent to about 30 inches of mercury, or 760 mm of mercury In reality, the pressure is equivalent to the height of the mercury barometer at the time of the experiment Pour a little mercury into the open leg The gas confined in the shorter leg diminishes in volume It is easy to prove that no gas has escaped from the shorter leg, and consequently, the gas in the shorter leg has been compressed, or is more closely packed than before In other words, the concentration of the gas per unit volume is increased by the pressure The difference in the levels of the mercury in the two legs plus the pressure of the atmosphere represents the pressure on the gas in the short leg More mercury may be poured in the longer leg, and thus a series of numbers are obtained representing the pressure and the volume of the gas in the closed limb When Boyle had poured sufficient mercury in the longer leg to reduce the volume of the gas in the shorter leg one-half he said "when we cast our eye on the longer leg, we observed, not without delight and satisfaction, that the quicksilver in the longer part was 29 inches higher than in the other" In other words, the volume was diminished one half when the pressure was doubled by superposing on to the ordinary pressure of the atmosphere, the pressure of a column of mercury 29 inches long and equal to the pressure of the atmosphere at the time of the experiment.

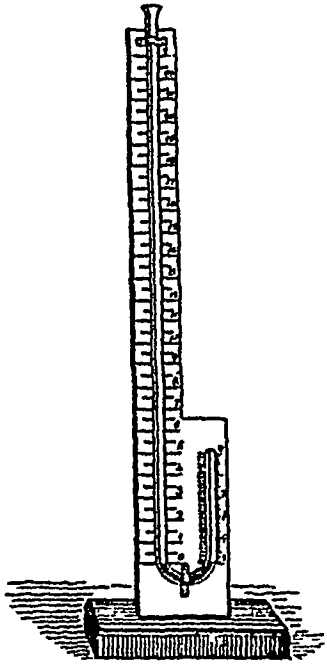


FIG 22 —Boyle's Law—High Pressures

To illustrate Boyle's important generalization, imagine 12 litres of a gas confined in a cylinder closed by a gas tight piston free to slide up and down the cylinder without friction Suppose further that the gas supports a weight of one atmosphere on the piston, *A*, Fig 23 If another equal weight be placed upon the piston, *B*, Fig 23, the gas will be compressed until it occupies a volume of six litres, another atmosphere pressure, *C*, Fig 23, will reduce the volume of the gas to 4 litres, and still another atmosphere pressure, *D*, Fig 23, will reduce the volume of the gas to 3 litres Collecting all these results into one table, we see that

Pressure	1,	2,	3,	4,	6 atmospheres
Volume	12,	6,	4,	3,	2 litres
Product pv	12,	12,	12,	12,	12

The law of Boyle may therefore be expressed another way The product of the pressure and the volume of a gas kept at one uniform temperature is always the same. Or,

$$pv = \text{Constant}$$

The numerical value of the constant, of course, depends upon what units are selected for representing the pressures and volumes. Pressures may be expressed in atmospheres, millimetres of mercury, pounds per square inch, etc , and the volumes in litres, cubic centimetres, cubic feet, etc.

Boyle's law assumes yet another guise If p_1 be the pressure of a gas occupying a volume v_1, and p the pressure when the volume is v,

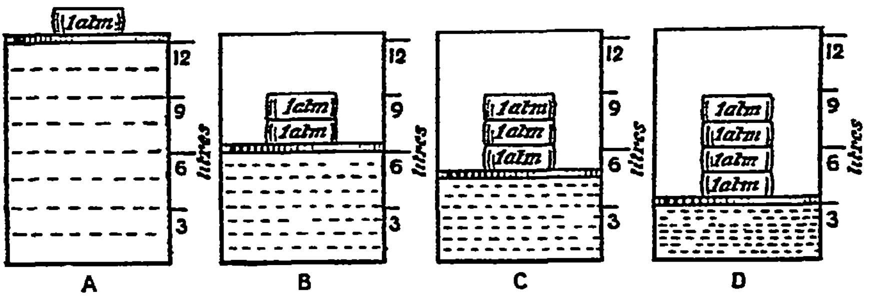


FIG 23 —Diagrammatic Illustration of Boyle's Law

then, since the products p_1v_1 and pv are equal to the same constant they are equal to one another Consequently,

$$pv = p_1v_1$$

If any three of these magnitudes be known, the fourth can be calculated directly

EXAMPLE —A eudiometer holds 4 5 litres of gas when the barometer read 755 mm What will be the volume of the same body of gas when the barometer stands at 760 mm.? Here $p_1=755$, $v_1=4\ 5$, $p=760$, hence, $v=4\ 47$ litres The most common problem is to calculate—" reduce "—the volume of a gas at any observed pressure to the corresponding volume at normal pressure 760 mm Given 4 5 litres of gas at 755 mm pressure, there is no need for any formula to calculate the corresponding volume at 760 mm The pressure 760 mm, is greater than 755 mm, hence the volume will be less, hence multiply 4 5 by the fraction $\frac{755}{760}$ and the result is 4 47 litres

Pressures less than atmospheric.—Boyle showed that the law holds good at pressures less than atmospheric Boyle used an arrangement similar in principle to that illustrated in Fig 24. Some mercury is poured into a narrow tube which is closed at one end, and open at the other The open end is closed by the thumb and inverted in the tall cylinder of mercury The narrow tube is raised or lowered, and the volume of gas confined in the narrow tube as well as the difference in the levels of the mercury in the narrow and in the wider tube read at the same time. We can recognize the principle of the U-tube, Fig 22, in this apparatus, Fig 24. The pressure on the mercury in the wide cylinder is one atmosphere, and the pressure of the gas in the narrow tube is one atmosphere less the pressure of a column of mercury equal to the difference in the level of the mercury in the two tubes

Measuring the volumes of gases—This arrangement illustrates a

problem which arises very often when the volume of a gas, collected over mercury, is to be measured. If the pressure of the atmosphere is 760 mm, and the difference in the levels of the mercury in the gas jar and in the pneumatic trough is 56 cm, it follows that the pressure of the gas in the narrow tube is 760 mm less 560 mm = 200 mm Whenever practicable, of course, the mercury inside and outside is brought to the same level before the gas is measured.

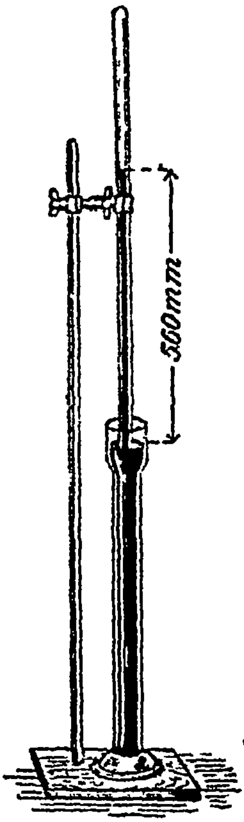


FIG 24 —Boyle's Law —Low Pressures

Suppose that the confining liquid is water, not mercury. Water is frequently used when the gases are not appreciably soluble in that liquid Suppose that the external pressure is 760 mm (barometer), and there is a difference of 10 cm between the level of the water confining the gas, and the level of the water exposed to the air The weight of 10 cm of water is not the same as the weight of 10 cm of mercury Mercury is 13 55 times as heavy as water, hence, a 10 cm. column of water is equivalent to the weight of a column of mercury $\frac{10}{13\ 55}$ or 0 74 cm. or 7 4 mm high The pressure of the gas is therefore $760 - 7\ 4 = 752\ 6$ mm. But water vapour exerts a definite pressure, and a still further reduction must be made if we want the pressure actually due to the gas and not to the mixture of vapour and gas. This will be investigated later

Test for the equilibrium of gases —If the gas be confined under such conditions that the product pv at any fixed temperature is not constant, the system will not be in a state of equilibrium If the piston, referred to in Fig 23, supports a weight of 6 atms. the gas must occupy a volume of 2 litres, if not, the gas will expand or contract until the product pv satisfies the test. Boyle's law describes the necessary condition for the volume and pressure of a gas to be in a state of equilibrium In practice there is no such thing as a frictionless piston, and if Boyle's law was to be tested in a real cylinder an allowance would have to be made for the friction of the piston by putting an extra weight on the cylinder The friction thus corresponds to what J W. Gibbs (1876) called the *passive resistance* of a system to assume a state of equilibrium The nature of the passive resistance can here be recognized, but in some cases we feel sure that something analogous retards the movement of a system to the condition called "stable equilibrium," although we know nothing of the character of the passive resistance or the hysteresis—from the Greek ὑστερέω (hystereo), I lag behind—which opposes the change.

§ 3 Deviations from Boyle's Law.

The pressures used by Boyle extended over a range varying from 3 cm. to 300 cm of mercury It is hazardous to infer that because the product pv is constant over a limited range of pressures, it will remain

constant for pressures widely different from those actually measured. The method of measurement used by Boyle, excellent for its time, is now considered somewhat crude. Many careful investigations have been made to find if the simple law of Boyle correctly describes the behaviour of gases at pressures far removed from the normal pressure of the atmosphere—76 cm of mercury. The general results show that no two gases behave precisely in the same way. The deviations for many gases are insignificant. With most gases, the concentration increases more, that is the volume increases less than Boyle's law describes, and at high pressures, the concentration increases less, that is the volume increases more than Boyle's law indicates. This is illustrated by plotting Boyle's law. Boyle's law, when graphed, furnishes the continuous curve shown in Fig. 25. This curve is a rectangular hyperbola. The deviations with nitrogen from this ideal condition are indicated by the dotted line in the same Fig. 25. According to Boyle's law, the volume of a gas should diminish indefinitely as the pressure is increased, and in time the volume would approach zero, that is absolutely nothing. This is absurd. Pressure can only diminish the space between the molecules and not the actual substance of the molecules. Hence, if b denotes the "volume" occupied by the molecules, the changes in the volume of the gas with variations of pressure will be represented by $p(v - b) =$ constant, not by $pv =$ constant.

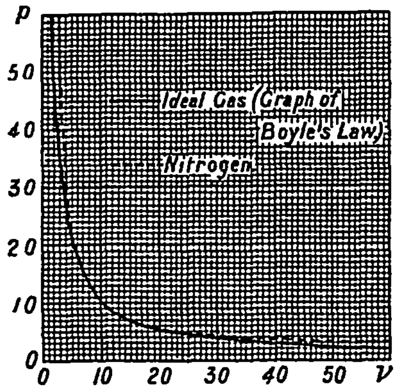


FIG. 25.—Volume pressure curves.

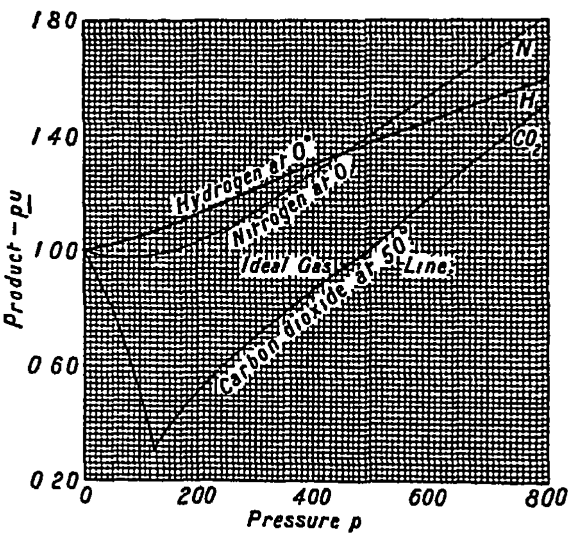


FIG. 26.—Pressure pv curves (Amagat).

It does not follow that b represents the actual volume of the space occupied by the matter in the molecules. This subject is taken up later. The effect of the "volume" of the molecules on the compressibility of a gas was recognized by D. Bernoulli, 1738; by M. W. Lomonossoff, 1750; by A. Dupré, 1865; and by J. D. van der Waals in 1872.

E. H. Amagat, 1893, showed that while the product pv remains fairly

constant at low pressures for many gases, the numerical value of pv changes in a remarkable manner as the pressures increase in magnitude Amagat's measurements for carbon dioxide show that when

p	1,	50,	100,	125,	150,	200,	500,	1000 atms
pv	1,	0 92,	0 49,	0 31,	0 41,	0 50,	1 02,	1 81

Notice how the product pv at first diminishes in magnitude and then steadily increases This is brought out very clearly on plotting the numbers If the products pv were constant for all values of p, we should get the straight line, dotted, and marked "ideal gas line" in Fig 26, with carbon dioxide, however, the curve descends below the line for an ideal gas, and then steadily rises, passing above the ideal gas line when the pressure is nearly 500 atmospheres.

The curves for hydrogen and helium, at ordinary temperatures, do not descend below the ideal gas line, but take a path resembling the hydrogen line shown in Fig 26 However, even these gases exhibit the same peculiar behaviour at lower temperatures Thus, with hydrogen at $-140°$, the product pv reaches a minimum when the pressure is about 25 atmospheres, at $-195°$, 45 atmospheres, and at $-213°$, 51 atmospheres It was once thought that oxygen behaved in a peculiar abnormal manner at a pressure of about 0 7 *mm* of *mercury*, but some careful measurements by Lord Rayleigh indicate that the statement is probably based upon a malobservation To summarize —

(1) With small pressures, the product pv decreases with increasing pressure showing that the volume with increasing pressure is less than is described by Boyle's law

(2) With large pressures, the product pv increases with increasing pressure, showing that the volume with increasing pressure is greater than is described by Boyle's law.

(3) All gases, in consequence, show a minimum value for the product pv The pressure corresponding with the minimum depends on the nature of the gas and on the temperature The minimum is less prominent with the more permanent gases[1] than with the more condensible gases

§ 4 Dalton's Law of Partial Pressures.

When two gases, which do not act chemically on one another, under the conditions of the experiment, are brought together, the gases mix intimately, by diffusion, so as to form an homogeneous mixture Furthermore, John Dalton (1802) found that each gas seemed to exert the same pressure as if it occupied the space alone, and the total pressure of the mixture of gases was the sum of the several pressures due to each gaseous component of the mixture If P be employed to denote the total pressure and p_1 the partial pressure exerted by one of the gases, and p_2 the partial pressure exerted by the other gas, Dalton's discovery means that $P = p_1 + p_2$ In words, in a mixture of gases which exert no physical or chemical action on one another, each gas exerts the same pressure as if it alone occupied the entire vessel, and the total pressure is

[1] Gases which "obey" Boyle's and Charles' Laws under ordinary atmospheric conditions usually remain gaseous at comparatively low temperatures and are accordingly called *permanent gases*

the sum of the partial pressures due to each gas This is Dalton's law of partial pressures. It is independent of Boyle's law, and can be extended to mixtures of any number of gases.

EXAMPLE.—Moist hydrogen gas is confined over water under a pressure of 760 mm of mercury at 10°, the partial pressure of water vapour at that temperature is 9 2 mm. of mercury Then from Dalton's law of partial pressures it follows that the hydrogen gas itself is under a partial pressure equivalent to 760 less 9 2, or 750 8 mm of mercury

It is highly probable that the molecules of nearly all gases exert some attractive influence on one another, and the gases will, in consequence of this *physical* action, "deviate" from Dalton's law to an extent dependent upon the magnitude of the intermolecular attraction Many mixtures of gases show slight, but marked deviations from the law *e.g* carbon dioxide and sulphur dioxide, hydrogen with air and with nitrogen, etc Accordingly, the theoretical results agree more closely with the observed results when an allowance is made for the effect of the attraction of the molecules for one another

The law has been applied to test if chemical action occurs on mixing certain gases, *e.g*, to find if any sign of chemical action occurs when nitric oxide (NO) is mixed with nitrogen peroxide (NO_2) resulting in the formation of nitrogen trioxide (N_2O_3) It is assumed that if no chemical combination takes place, the mixture will obey Dalton's law, and conversely In cases like this, it is assumed that the molecules of the two gases exert neither attractive nor repulsive forces upon one another If they did, the test might lead to wrong conclusions with respect to chemical action. A slight contraction, for instance, might be evidence of molecular attraction, not of chemical combination.

§ 5 The Laws of Nature.

We must confess that physical laws have greatly fallen off in dignity No long time ago they were quite commonly described as the Fixed Laws of Nature, and were supposed sufficient in themselves to govern the universe Now we can only assign to them the humble rank of mere descriptions, often erroneous, of similarities which we believe we have discovered —J H. POYNTING

This is a convenient place to further emphasize the meaning of the term "law" in chemistry It is of course absurd to say that Dalton's law or Boyle's law *must* be obeyed, implying that these laws are commands imposed upon gases which they are compelled to obey "Law" is a useful term which the careless sometimes personify It is employed by scientific men, purely in a metaphorical sense The term has led to some confusion, and it would be replaced by another word, if we could think of a better The German equivalent—*Gesetz*, statute—is perhaps worse As indicated previously, the term "law of nature" is applied to a comprehensive generalization which "methodically and systematically describes certain natural phenomena" The laws of chemical and physical phenomena are collocations of those circumstances which have been found by experiment and observation to accompany all chemical and physical changes included in the statement of the law The test of the "law" is that the statement holds good without exception The common meaning attached to the saying, "The exception proves the rule," is wrong, and

it is an instance of confusion arising from the double meaning of words In the old Latin form *Exceptio probat regulam*, the word "probat" means "tests," just as to-day, "proving wines" means testing them The proverb therefore meant that the exception *tries tests, or proves* the rule, and if the exception cannot be explained, then the rule breaks down, for the exception disproves the rule When the exact conditions are set up, the law describes the phenomenon without variableness or shadow of turning The law is then regarded as an objective power This power is called a force, and further, the force is said to be the cause of the phenomenon. Thus gravitation is regarded as an attractive force causing one particle to attract every other particle in the universe; chemical affinity is regarded, in this sense, as a selective force which causes certain substances when placed in contact to undergo chemical change If therefore we find a gas deviating from Boyle's law, or a mixture of gases "disobeying" Dalton's law, the alleged laws may be false, incomplete, or imperfect descriptions, or some perturbing influence is at work which masks the simple phenomena described by these laws

§ 6 The Influence of Temperature on the Volume of Gases—Charles' Law.

In 1790, Joseph Priestley concluded "from a very coarse experiment" *that* "fixed and common air expanded alike with the same degree of heat" and J L. Gay-Lussac, in 1802,[1] quoted some experiments in support of the broader view The same rise of temperature produces in all gases the same increase in volume, provided the pressure be kept constant. This *law is designated* Charles' *law, in honour of* J A C Charles, who, according to Gay-Lussac, made some crude experiments on the subject fifteen years before Gay-Lussac's publication Some call this relation "Gay-Lussac's law"

The increase in volume which occurs when one litre of nitrogen at 0° is heated in a suitable vessel is shown in the following table (R. Chappius, 1888) —

Temperature $\theta°$	Volume v litres	Expansion per litre per degree
0	1 00000000	
10	1 00367781	0 00036778
20	1 00735306	0 00036776
30	1 01102875	0 00036775
40	1 01470244	0 00036737

The numbers in the last column—called the coefficients of thermal expansion—mean that the volume v of a litre of nitrogen, when heated through $\theta°$ can be represented very closely by the expression $v = (1 + 0\ 0036760)$ litres In other words, nitrogen increases 0 003676, or very nearly $\frac{1}{273}$ part of its volume at 0° for every degree rise of

[1] John Dalton published an account on some experiments on gases, in 1802, but Dalton's statement of the action of heat is not quite right. G Amontons had an inkling of this law in 1702

temperature More generally, if v_0 be used to denote the volume of a gas at 0°, we have, instead of the preceding expression,

$$v = v_0\left(1 + \frac{\theta}{273}\right)$$

This is very nearly true for most of the common gases, and it therefore represents a condition of equilibrium which must be satisfied by the temperature and volume of a gas, under constant pressure, in order that the system may be in stable equilibrium.

While solids and liquids have their own characteristic coefficient of expansion, gases have nearly the same coefficient of thermal expansion. This is the meaning of Charles' law The coefficients for the gases run something like this —

Air	0 003665
Hydrogen	0 003667
Carbon dioxide	0 003688

These numbers are close enough to "$\frac{1}{273}$" for most practical purposes. In general, the more easily a gas is liquefied, the greater the deviation from the constant 0 003665 found for air—witness carbon dioxide.

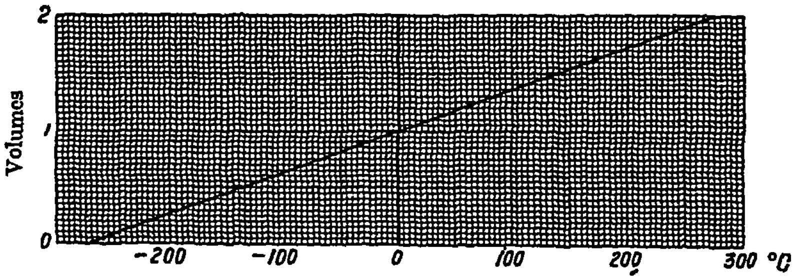


FIG 27 —Graph of Charles' Law

By plotting the above equation, we get the curve shown in Fig 27 If the temperature be less than −273°, the gas would have a negative volume, that is a volume less than nothing! If the temperature be −273°, the gas would occupy no volume! It is impossible to imagine a substance occupying no space, but such is a logical conclusion from Charles' law Where is the fallacy? Whenever a natural process is represented by mathematical symbols, it is well to remember that the artificial statement often expresses more than actually obtains in nature, because, in the physical world, only changes of a certain kind occur We must therefore limit the generality of the mathematical expression Charles' law includes a simplifying assumption The apparent volume of a gas may be resolved into at least two parts (1) the "volume" occupied by the molecules of the gas, and (2) the space between the molecules Although, for the sake of simplicity, we assume v is employed to represent the *total volume* occupied by the gas, in reality v should refer only to the space between the molecules, and in that case, the conclusion that $v = 0$ when the temperature is −273° involves no absurdity Moreover the gas would liquefy before the temperature −273° was attained, and the simple gas law of Charles would not then be applicable

The temperature −273° C is supposed to be a limiting temperature—

the nadir or lowest possible temperature Hence, it is sometimes called the absolute zero, and temperatures reckoned from this zero are called absolute temperatures On the absolute scale of temperatures, 0° C will be 273° abs If T be employed to denote the temperature on the absolute scale, and θ the temperature on the centigrade scale, we have $T = 273 + \theta$ Hence, we see that if v be the volume of a gas when the absolute temperature is T, and v_1 the volume when the temperature is T_1, we get, from the preceding equation,

$$\frac{v}{T} = \frac{v_1}{T_1}$$

which is but another way of stating Charles' law

§ 7 The Combined Influence of Temperature and Pressure on the Volume of a Gas

According to Boyle's law, the volume varies inversely as the pressure, and according to Charles' law, the volume varies directly as the absolute temperature, then it follows[1] at once that when both temperature and pressure vary, the effect on the volume will be given by the equation

$$pv = RT$$

where R is the constant of proportion—generally called the gas constant This important relation is sometimes called *Clapeyron's equation* The same result can be expressed another way If p, v, and T respectively denote the pressure, volume, and absolute temperature of a gas under one set of conditions, and p_1, v_1, and T_1 the pressure, volume, and absolute temperature under another set of conditions, then

$$\frac{pv}{T} = \frac{p_1 v_1}{T_1}$$

This formula is used a great deal in calculations involving the variations in the volumes of gases owing to variations in temperature and pressure For instance in reducing the volume of a gas at any observed temperature and pressure to the corresponding volume at normal temperature and pressure —0° C and 760 mm. pressure—often represented by "n p t", or "N P T", or "S T P.", or "S T, S P"

EXAMPLE —If a gas measures 170 c c at a pressure of 735 mm mercury, and a temperature of 15°, what is the volume of the gas at normal temperature and pressure? Here it is required to find v in the preceding formula where $p = 760$, $T = 273$, $T_1 = 288$, $v_1 = 170$, and $p_1 = 735$, hence, $v = \frac{273}{288} \times \frac{735}{760} \times 170 = 155.8$ c c.

§ 8 Deviations from Charles' Law

We have already seen that the coefficients of thermal expansion of all gases are only approximately the same The coefficients for the individual gases differ a little among themselves as indicated above The variation in the coefficient of thermal expansion at temperatures and pressures, not far removed from normal atmospheric temperatures and pressures, is not very marked, and for regular gas calculations can be ignored It remains to indicate the variation, if any, in the coefficient of thermal expansion with large variations of temperature and pressure

[1] It is shown in elementary text-books in algebra that when x varies inversely as y, and x varies directly as z, then $xy = kz$ where k is the constant of proportion

1 The influence of pressure —The coefficient of expansion of most gases is increased by augmenting the pressure of a gas until a maximum value is attained, after that, the coefficient diminishes with increased pressure. For instance, E H. Amagat (1893) found that the coefficients of expansion of carbon dioxide at temperatures between 50° and 60° assumed the following values —

Pressure	30,	60,	125,	200,	500,	1000 atm
Coefficients	0 0069,	0 0085,	0 0410,	0 0085,	0 0033,	0 0018

Carbon dioxide thus shows a marked variation in the coefficient of thermal expansion at high pressures In agreement with these facts, the coefficient also diminishes as the pressure is reduced even so low as 0 077 mm of mercury The variation is not so marked with gases like nitrogen, oxygen, and hydrogen which are not easily condensed to the liquid condition The value of p which furnishes the greatest coefficient of thermal expansion is that same value of p which gives the minimum product pv, p 81 At ordinary temperatures, therefore, hydrogen and helium do not exhibit this variation in the value of their coefficients of expansion With these gases, the coefficient of expansion steadily diminishes with increasing pressure

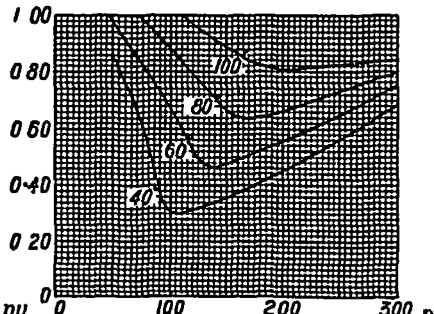


Fig 28 —Amagat's Curves for Carbon Dioxide

2 The influence of temperature. — The maximum value for the coefficient of expansion with increasing pressure just indicated becomes less and less as the temperature is raised and finally disappears So does the minimum value of the product pv become less and less marked as the temperature is raised The gradual "flattening" of the carbon dioxide curves as the temperature rises from 40° to 100° is brought out very clearly in Fig 28 We have seen p 81, that all gases exhibit the minimum value for pv The pressure required for the minimum depends on the temperature as well as on the nature of the gas The minimum is most marked when the gas is near its critical temperature (p 81) If the temperature is much above the critical temperature, the minimum is very small—with hydrogen the minimum is inappreciable at 0°—Fig 26 All other gases show a minimum at ordinary temperatures Hence, Regnault, who discovered this phenomenon, was led to say that hydrogen is a "gaz plus que parfait" But hydrogen also shows the minimum at reduced temperatures as indicated on p 81

9 Methods for Measuring the Vapour Densities of Gases and Volatile Liquids and Solids

Since determinations of molecular weights are usually made to decide between quantities widely different, minor corrections, necessary for exact values, are not required. For instance, if chemical analysis showed that the molecular weight of a compound is some multiple of 20, then a molecular weight of 83, by vapour density methods indicates that

$4 \times 20 = 80$ is the molecular weight of the body Corrections for the expansion of glass with temperature, the deviation of the weight of a cubic centimetre of water from one gram, the deviation of the vapour from a perfect gas in calculating the volume at normal temperature and pressure, etc, may be neglected

I. Gases at Ordinary Temperatures

In measuring the relative density of a substance which is gaseous at ordinary temperatures, a large gas balloon of known volume v is counterpoised on the balance by a similar second balloon of approximately the same volume so as to eliminate corrections necessary for the buoyancy of the air By repeated exhaustions and re fillings the balloon is filled with the gas under investigation The temperature and pressure are respectively t and p Let w denote the difference between the weights of the full and empty balloon The volume v_0 of the gas at 0° and 760 mm pressure is calculated in the ordinary manner p 85:

$$v_0 = v \frac{p}{760} \frac{273}{273 + t}, \text{ or } v_0 = 0.3592 \frac{vp}{273 + t} \quad . \quad . \qquad (3)$$

The corrections needed for very exact density determinations need not be here considered since they do not affect the general principle From Avogadro s hypothesis the molecular weight of a gas represents the weight of 22 3 litres of the gas if hydrogen = 2 be taken as the standard Consequently, if w grams of a gas occupy v_0 c.c at 0° and 760 mm pressure, 22,300 c c will weigh $22\,300\, w \div v_0$ grms, and this represents the molecular weight, or the relative density of the gas, hydrogen = 2

EXAMPLE —585 c.c of carbon dioxide measured at 18° and 756 mm pressure, weighed 1 076 gram What is the molecular weight of the gas? From (3), the 585 c c of gas become, at 0° and 760 mm, 546 1 c c Hence, the molecular weight, is $22{,}300 \times 1\,076 \div 546\,1 = 43\,9$

II. Solids and Liquids which can be Vaporized without Decomposition

A From the Weight of a Known Volume of the Vapour

(1) *J. B Dumas' process* (1826) —A light glass bulb, *A*, Fig 29, between 100 and 200 c c capacity is weighed, and from 6 to 10 grams of the compound under investigation are introduced into the bulb By means of a suitable clamp, *D*, the bulb is fixed in a suitable bath, *B*, at a constant temperature 20° to 30° above the boiling-point of the compound under investigation The compound vaporizes, and when its vapour ceases to issue from the neck, *C*, of the bulb, the tube is sealed at *C* by means of a blowpipe with a small flame The temperature of the bath at the time of sealing is the average between the two thermometers *T*, the barometric pressure is read at the same time The bulb is then cooled, cleaned, and weighed The volume of the bulb is now determined by breaking the tip, *C*, of the neck under water or mercury, and weighing the bulb when full

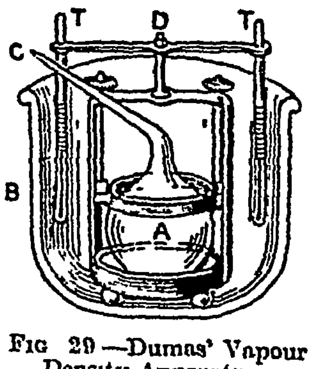


FIG 29 —Dumas' Vapour Density Apparatus

of liquid[1] The difference between the full and empty bulbs gives the amount of liquid in the bulb The application of the data can be best illustrated by example

EXAMPLE —The following data were obtained for vanadium tetrachloride, VCl_4

Weight of globe filled with air (9°, 760 mm)	24 4722 grams
Weight of sealed globe (9°, 760 mm)	25 0102 grams
Temperature of bath when sealing the globe	215°
Barometer when sealing the globe	762 mm
Weight of bulb full of water	194 grams

The globe held 194 less 24 4722 = 169 5 grams of water at 9° This represents very nearly 169 5 c c of water, or the capacity of the globe is 169 5 c c The apparent weight of the substance at 9° is 25 0102 − 24 4722 = 0 538 gram The empty globe was buoyed up, during weighing, by its own bulk of air at 9° and 762 mm , and since 1 c c. of air at N P T weighs 0 001293 gram, 169 5 c c of air at 9° and 762 mm weigh, at N P T (0 001293 × 169 5 × 273 × 762) ÷ (760 × 282) = 0 213 gram This added to 0 538 gram, gives 0 751 gram, the weight of the vapour in the globe at the time of sealing The 0 751 gram of vapour occupied 169 5 c c at 215° and 762 mm pressure, or 95 10 c c at 0° and 760 mm pressure Hence, 22,300 c c. of vapour at normal temperature and pressure weigh 176 1 grams This number also represents the molecular weight of vanadium chloride

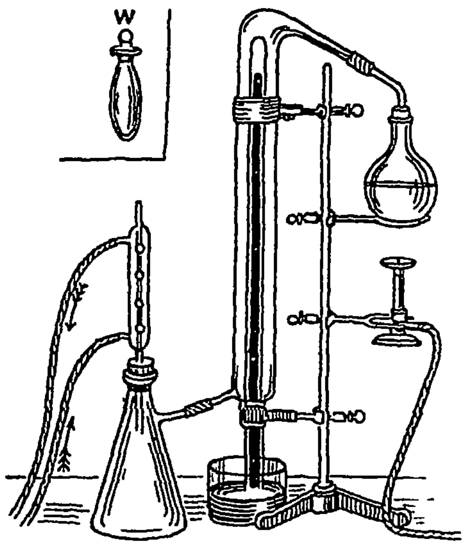


FIG 30 —Hofmann's Vapour Density Apparatus

The objection to Dumas' process is the amount of material required to drive out the air from the bulb This waste is avoided in the two succeeding methods — Hofmann's and Meyer's processes. By using porcelain or platinum vessels, Dumas' process has been employed for bodies volatilizing at high temperatures

(2) *A W Hofmann's process* (1868) —This is a modification of an earlier method due to J L Gay Lussac (1811) A known weight of the substance in a small stoppered glass bulb, shown on an enlarged scale at *W*, Fig 30, is taken The bulb is introduced below a barometer tube filled with mercury, and surrounded with a jacket through which the vapour of a liquid, which boils about 20° above the boiling point of the compound under investigation, is passing The bulb ascends to the upper level of the mercury, and the substance is thus vaporized under a reduced pressure The volume of the vapour is read when everything is in

[1] If the globe contains residual air, a correction must be made The volume of the vapour will be equal to the volume of the globe, less the volume of the residual air , and the weight of the vapour will be this difference plus the buoyancy of a quantity of air at t and p of the second weighing, equal to the volume of the vapour

equilibrium, the height of the barometer, and the temperature of the apparatus are also read

EXAMPLE.—The following data were obtained for carbon tetrachloride, CCl_4

Weight of liquid in bulb	0.3380 grm
Volume of vapour	109.8 c.c
Temperature of vapour	99.5°
Barometer	746.9 mm
Height of mercury in tube	283.4 mm

The pressure of the vapour, as we shall see very shortly, is the barometric height less the height of the column of mercury in the Hofmann's tube, that is, 746.9 − 283.4 = 463.5 mm. Hence, 0.3380 gram of vapour at 99.5° and 463.5 mm pressure occupy 109.8 c.c, and 49.09 c.c at 0° and 760 mm. Hence, 22,300 c.c of the vapour at normal temperature and pressure weigh 153.6 grams, and this number represents the molecular weight of carbon tetrachloride

Hofmann's process is useful when only a small amount of the substance is available for a determination, and for substances which decompose when heated at a temperature in the vicinity of their boiling point at ordinary atmospheric pressures ✓

B. From the Volume of a Known Weight of the Vapour

V. Meyer's process.—V and C Meyer (1877) described an elegant and simple method of finding the volume of a vapour by measuring the volume of air displaced by a given weight of the substance vaporized in a suitable vessel. The following is a modification of Meyer's process. A bulb—about 200 c.c capacity—has a long neck fitted with a side tube leading to a gas measuring burette, *B*, Fig 31. An arrangement, *A*, is fitted to the long neck so that when *A* is turned half a revolution, a small stoppered bottle—shown on an enlarged scale at *W*, Fig 30—can be dropped down the long neck into the heated bulb, which has a little glass wool or asbestos on the bottom, so that the falling bulb will not break the apparatus. A three-way cock, *D*, is turned so as to connect the bulb with the air. The inner chamber is heated by the vapour of a substance placed in the vapour jacket. The substance in the vapour jacket *E* is chosen so that it boils 20° or 30° above the boiling-point of the compound under investigation. The vapour jacket, *E*, is protected in turn by a metal jacket, *F*. When everything is in position the mercury in the gas burette at zero, the temperature of the vessel constant, and the bulb at *A*, containing a

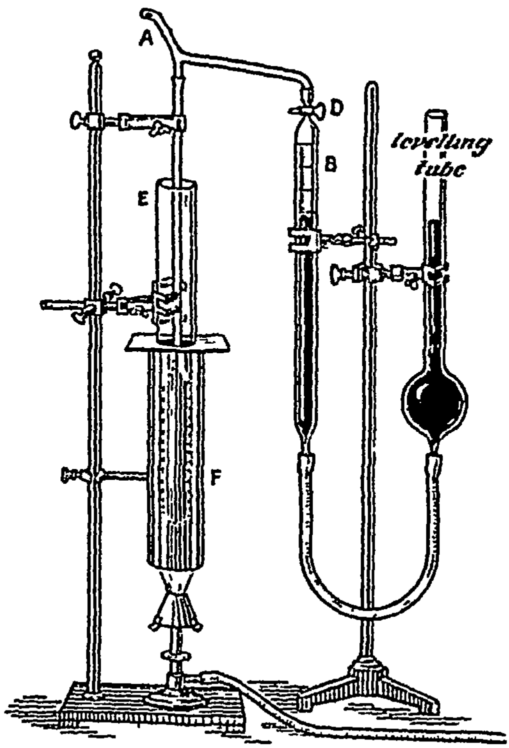


FIG 31.—Meyer's Vapour Density Apparatus

weighed amount of the compound under investigation, is ready to be dropped into the inner chamber, the three way cock connecting the bulb tube with the atmosphere is turned in order to connect the apparatus with the gas burette The tube W is dropped from A The vapour of the compound displaces its own volume of air, and the displaced air collects in the gas burette. When air has ceased to collect in the gas burette, and the mercury in the levelling and measuring tubes is at the same level, the cock is closed When the gas burette has had time to attain the temperature of the room, the mercury in the measuring and levelling tubes is again adjusted to the same level, and the volume of air which has collected in the burette is noted. The temperature and the barometer are read at the same time.

EXAMPLE —The vapour density of water was determined, and the following data were obtained Xylene, boiling at about 138°, was used in the hot jacket E —

Weight of water in the stoppered tube W	0 0102 gram
Temperature of gas in burette	16 5°
Barometer	703 8 mm
Volume of gas	16 6 c.c.

The 16 6 c c of vapour at 16 5° and 703 8 mm becomes 14 496 c c at 0° and 760 mm This is the volume of 0 0102 gram of vapour Hence 22,300 c c of the vapour will weigh 15 7 grams This number represents the molecular weight of water vapour

Questions

1 State how the volume of a gas is related to temperature and pressure. Describe experiments in illustration of your answer A gas measures five litres at 20° C, and 770 mm mercury pressure What will be its volume at 5° C, and under a pressure of 750 mm of mercury ?—*Aberdeen Univ*

2 A barometer tube has some air in the space above the mercury The height of the column is found to be 29¼ inches when it ought to be 30 inches and 30 when it ought to be 31 What ought it to be when it reads 29 ?—*Aberystwyth Univ*

3 Describe very briefly the principles on which the chief methods for measuring vapour densities are based What factors determine the choice of one method over others in practice ? The vapour density of a substance was determined in two ways A bulb holding 124 c c was sealed up when filled with the vapour at 99° C and 760 mm. The weight of the vapour was found to be 0 3276 gram In the second experiment, 0 1 gram of the substance displaced 28 c c of air (corrected) in V Meyer's apparatus Calculate the vapour density given by the two experiments if 1 litre of hydrogen N T P weighs 0 09 gram —*Owens Coll*

4 0 25 gram of a liquid gave 62 c c of vapour measured at 98° C, bar 740 mm The mercury in the measuring tube standing 140 mm above the mercury in the trough What was the density of the vapour compared with that of hydrogen ? —*New Zealand Univ*

5 Explain clearly why temperature and pressure observations are necessary when measuring the volume of gases

6 If a quantity of nitrogen under 900 mm pressure at 20° occupies a volume of 700 c c, what volume will it occupy at 100°, under a pressure of 600 mm. pressure ?—*Cornell Univ*

7 250 c c of oxygen at 10° and 756 mm Find the volume at 0° and 760 mm —*Mason Science Coll*

8 If a quantity of hydrogen occupies 500 c c in a tube over mercury, the level within the tube being 70 mm above that, the temperature being 40°, and the barometric pressure 740 mm, what volume will it occupy at S T P (standard temperature and pressure) ?

CHAPTER VI

Hydrogen

Atomic weight, H = 1·008; molecular weight, H_2 = 2·016; univalent. Melting point, −259°; boiling point, −252·5; critical temperature, −241°. Relative vapour density (H_2 = 2), 2; (air = 1) 0·0696; one litre of hydrogen, at 0°, 760 mm. pressure, and latitude 45° at sea-level, weighs 0·08995 (sometimes called a *crith*); and one gram occupies 11·117 litres.

§ 1 Hydrogen—Occurrence

The element hydrogen occurs free in nature in comparatively small quantities. The atmosphere is said to contain about one volume of hydrogen per 15,000 to 20,000 volumes of air. Hydrogen is also present in volcanic gases; in the gases from the Stassfurt salt beds; and in some meteorites. The presence of hydrogen in natural gas from the oil fields has been denied, although many published analyses of these gases include "hydrogen." The sun's chromosphere shows what appear to be stupendous flames of incandescent hydrogen, in some cases towering over 300,000 miles (M. Fényi, 1892) into space, and 100,000 miles in width (C. A. Young, 1872)—thousands of times larger than the earth on which we live. Spectroscopic observations also show that hydrogen is present in nebulæ and certain stars.

Combined hydrogen is common. Water contains one-ninth of its weight of hydrogen. We really know nothing about the hydrogen as it is combined with oxygen in water. The fact is that when water is decomposed under certain conditions, this proportion of hydrogen is obtained. It is the *façon parler* to say that the compound "*contains*" the element, or that the element "*occurs*" in or is "*present*" in the compound, when the element can be obtained from the compound by suitable methods of decomposition. Hydrogen, together with oxygen, is one of the chief constituents of animal and vegetable tissue. Hydrogen also is present in nearly all organic compounds, and in many gases—methane, the hydrocarbons, hydrogen sulphide, etc.

Quantitative distribution of the elements.—By comparing a large number of analyses of rocks, etc., F. W. Clarke (1908) has tried to estimate the percentage composition—by weight—of the earth's crust (½ mile deep)—including the ocean and the atmosphere. His result is:

	Per cent		Per cent		Per cent
Oxygen	49·78	Magnesium	2·24	Barium	0·09
Silicon	26·08	Hydrogen	0·95	Manganese	0·07
Aluminium	7·34	Titanium	0·37	Strontium	0·03
Iron	4·11	Chlorine	0·21	Nitrogen	0·02
Calcium	3·19	Carbon	0·19	Fluorine	0·02
Sodium	2·33	Phosphorus	0·11	Bromine	0·008
Potassium	2·28	Sulphur	0·11	All other elements	0·48

If we try to get an estimate of the *relative* number of atoms of the different *kinds* of elements distributed in the half-mile crust, the ocean and the atmosphere, Clarke's numbers must be divided by the corresponding atomic weights of the elements We thus obtain for the percentage number of atoms in the half-mile crust

Oxygen	53 81	Sodium	1 72	Potassium	1 02
Hydrogen	16 30	Magnesium	1 61	Carbon	0 27
Silicon	15 87	Calcium	1 40	Titanium	0 16
Aluminium	4 68	Iron	1 29	Chlorine	0 11

This gives a better idea of the relative distribution of the elements from the chemical point of view than the actual weights in the preceding list

§ 2 The Preparation of Hydrogen.

We have seen in Chapter III. how hydrogen is produced by the action of metals on water or steam. The black oxide of iron produced in the reaction has the empirical formula Fe_3O_4 The action of steam on metallic iron is represented by the equation $3Fe + 4H_2O = Fe_3O_4 + 4H_2$ This process is used on a large scale Porous briquettes of iron are sometimes employed. These are made from the "spent" pyrites obtained as a by-product in the manufacture of sulphuric acid.

The action of sodium on water (p 50) is represented by the equation.

$$2Na + 2\begin{matrix}H\\H\end{matrix}\!\!>O = 2\begin{matrix}Na\\H\end{matrix}\!\!>O + H_2$$

where one atom of hydrogen in the molecule of water is replaced by an atom of sodium, whereby a solution of sodium hydroxide—NaOH—and hydrogen gas are formed An alloy of sodium with lead—called commercially "hydrone"—generates hydrogen very satisfactorily when in contact with water The same remark applies to aluminium amalgam—called commercially, "hydrogenite" See "hydrolith," p 104. The reactions between iron, zinc, and magnesium with sulphuric or hydrochloric acids (p 42) are represented

$$M^{II} + H_2SO_4 = MSO_4 + H_2, \text{ and } M^{II} + 2HCl = MCl_2 + H_2$$

where M^{II} stands in place of the bivalent metal Fe, Zn, or Mg

In these examples, it will be observed that the process of chemical change results in the substitution of the two atoms of hydrogen in the acid by an equivalent atom of Zn, Fe, or Mg In the last reaction with zinc and sulphuric acid, for example, zinc sulphate—$ZnSO_4 7H_2O$—can be obtained as indicated previously Similarly by evaporating the solution remaining after the action of sodium on water, sodium hydroxide—NaOH—is obtained, and with potassium potassium hydroxide—KOH.

The progress of aeronautics has considerably increased the technical importance of hydrogen In addition to the methods of preparing hydrogen on a large scale, discussed in Chapter III, a fairly pure gas can be obtained by warming aluminium or zinc with a dilute solution of sodium hydroxide (50 grms of the hydroxide per 500 c c of water) The reaction is represented

$$2Al^{III} + 2\left\{\begin{matrix}NaOH\\NaOH\\NaOH\end{matrix}\right. = 2Al\begin{matrix}\diagup ONa\\ -ONa\\ \diagdown ONa\end{matrix} + 3H_2, \text{ and } Zn^{II} + \begin{matrix}NaOH\\NaOH\end{matrix} = Zn\!<\!\begin{matrix}ONa\\ONa\end{matrix} + H_2$$

Here it will be observed that the hydrogen atoms in sodium hydroxide are replaced by the respective elements, and sodium aluminate, $Al(ONa)_3$, is a by-product in the former process, and sodium zincate, $Zn(ONa)_2$, in the latter case We see therefore, that under the stated conditions, an atom of sodium or potassium can displace only one of the two hydrogen atoms in the water molecule—H_2O, and that zinc or aluminium can displace the other hydrogen atom

The preparation of hydrogen by the action of sodium hydroxide on the element silicon has been patented The reaction is represented by the equation $Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2$, and also by $Si + 4NaOH = Na_4SiO_4 + 2H_2$ But only 80 per cent of the available hydrogen is obtained before the reaction begins to slow down. If, however, some calcium hydroxide be mixed with the sodium hydroxide, the process appears to be quite satisfactory 0 8 kilogram of silicon with 1 2 kilogram of alkali will give, in practice, a cubic metre of hydrogen

Hydrogen is a by-product in the manufacture of chlorine by the electrolysis of aqueous solutions of alkali chlorides $2NaCl + 2H_2O = 2NaOH + H_2 + Cl_2$ Chlorine is given off at one electrode and hydrogen at the other The sodium chloride is broken down by the electric current into sodium and chlorine, and the sodium in contact with water, reacts as indicated above $2Na + 2H_2O = 2NaOH + H_2$

Hydrogen and oxygen can be manufactured on a commercial scale, where electric power is cheap, by the electrolysis of aqueous solutions—acidulated water, etc —under such conditions that the hydrogen and oxygen are kept separate from each other The gases are separately compressed in steel cylinders—called "bombs"—under a pressure of about 100 or 150 atmospheres [1]

§ 3 The Hydrogen Equivalent of the Metals

It is interesting to determine what quantities of the different metals are chemically equivalent to one gram of hydrogen This can be done by dissolving the different metals in different acids [2] A pair of tubes—Hempel's gas burette—*A* and *B*, Fig 32, are arranged as shown in the diagram *C* is a flask containing the necessary acid—cold—and a weighed amount of metal The metal is contained in a test tube in the flask and left there until the necessary adjustments have been made The levelling tube *B* is raised until the water in *A* is at zero, and on the same level as the water in the levelling tube *B* The water in the levelling tube should be nearly at the bottom of the tube The flask is closed with a rubber stopper Raise or lower *B* until the level of liquid in the tubes is the same Read the level of the liquid in *A* The flask is then tilted so that the metal comes in contact with the acid, and the levelling tube is lowered at the same time

[1] The cylinders of hydrogen are often coloured red to prevent accidentally using a cylinder of hydrogen for one of oxygen

[2] Zinc in dilute sulphuric acid (1 7) The strength of dilute acid is often represented by numbers in this way The numbers mean that one volume of the concentrated acid is mixed with 7 volumes of water The strength of the commercial acids varies within narrow limits Magnesium is dissolved in dilute sulphuric acid (1 30), in dilute hydrochloric acid (1 7), aluminium in warm dilute hydrochloric acid (1 3), aluminium in warm dilute sodium hydroxide (50 grms sodium hydroxide, 500 c c of water) There are numerous other ways of doing the experiment besides that described in the text

When all the metal has dissolved, and the apparatus has had time to cool to the temperature of the room, bring the liquid in the tubes *A* and *B* to the same level by raising or lowering *B*. Read the volume of the gas, the thermometer, and the barometer. Calculate the weight of the hydrogen corresponding with the measured volume of hydrogen, and finally express the result in terms of one gram of hydrogen.

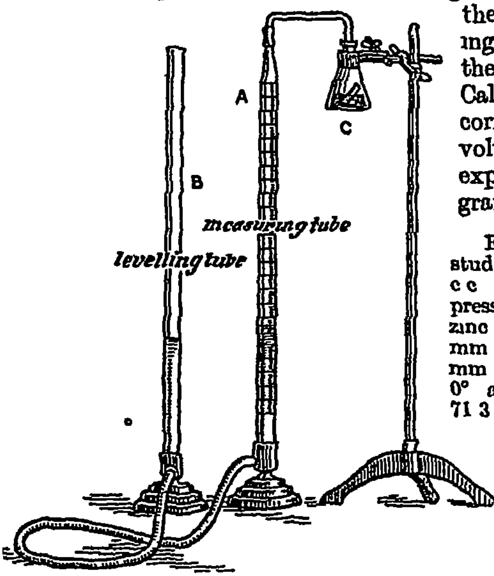


FIG. 32.—The Hydrogen Equivalent of the Metals.

EXAMPLE.—In an experiment by a student, 0.2 grm. of zinc gave 75.5 c.c. of hydrogen, at 15° and 758 mm. pressure. What is the equivalent of zinc? Here 75.5 c.c. at 15° and 758 mm. become 71.3 c.c. at 0° and 760 mm. Since 22.3 litres of hydrogen at 0° and 760 mm. weigh 2.016 grms., 71.3 c.c. of hydrogen will weigh 0.00645 grm. This weight of hydrogen comes from 0.2 grm. of zinc, hence 32.25 grms. of zinc are equivalent to one grm. of hydrogen.

One gram of a given metal will always displace the same amount of hydrogen whatever be the liquid used—*e.g.*, aluminium in sodium hydroxide, in sulphuric acid, or in hydrochloric acid; but the amounts furnished by different metals are different. The weight of a metal required to displace one gram of hydrogen is called the hydrogen equivalent, or the chemical equivalent of the metal. The following numbers for the chemical equivalents of three metals are taken from student's note books:

Zinc, 32.48; magnesium, 12.14; aluminium, 8.96.

These numbers agree closely with those obtained for these metals when referred to the standard oxygen = 8, p. 14.

§ 4. Chemical Affinity.

There are agents in nature able to make the particles of bodies stick together by very strong attractions. And it is the business of experimental philosophy to find them out.—ISAAC NEWTON.

The cause of chemical action has mystified man from the earliest ages, and there is no prospect of an immediate solution. Matter appears to be endowed with properties in virtue of which two or more dissimilar substances, when brought into contact, give rise to other forms of matter possessing properties quite distinct from the original substances. The process of change is called a chemical reaction. At present, *chemical action can only be referred back to the presence of selective forces, indwelling in the different kinds of matter, which lead certain substances, under certain conditions, to undergo chemical change.* This selective force is called

"chemical affinity" Chemists are chary about using the term "chemical affinity" because it suggests that elements, etc, combine or react because of a relationship, kinship, or family tie The elements fluorine, chlorine, bromine, and iodine, for instance, are said to have a "family relationship" or "natural affinity" for each other As a matter of fact, elements related in this sense do not usually form stable compounds On general principles it is well to avoid terms which are not clear and precise in meaning, and which are liable to misunderstanding, because they are not always understood in the same way by everybody.[1] In chemistry, however, the term "affinity" is reserved to connote not a "resemblance" but a tendency of the different kinds of matter to unite with one another H. Boerhaave used the term in this sense in 1732, and he metaphorically compared the force of affinity with "love, if love be the desire for marriage"[2] We must allow, said J B Dumas (1837), that "there is some truth in this poetic comparison" Hence, the term "affinity" is used by chemists in a metaphorical sense for that peculiar force or form of energy which is the origin of all chemical changes

Chemical affinity is conveniently regarded as "the driving force of a chemical reaction" In 1887, W E Ayrton and J Perry expressed the idea that

$$\text{Reaction velocity} = \frac{\text{Driving force}}{\text{Resistance}}$$

Consequently, if we could measure the chemical resistance offered by substances to undergo chemical change, it would be possible to get a definite and quantitative idea of chemical affinity from measurements on the velocity of a reaction No real advance can be made in the study of chemical affinity until a method of measurement has been devised

§ 5. The Measurement of the Affinity between the Acids and the Metals

> I often say that if you can measure that of which you speak, and can express it by a number, you know something of your subject, but if you cannot measure it, your knowledge is meagre and unsatisfactory —LORD KELVIN

The relation between the velocity and the driving force of a moving body—If a ball be sent rolling with a velocity of 20 cm per second, the force applied to the ball will be twice as great as would be required to make the ball travel with a velocity of 10 cm per second during the same time Neglecting friction, the intensities of the two forces are proportional to the velocities which they impart to each mass during the same time

The relation between the speed of a chemical reaction and affinity.—C F Wenzel, 1777, tried to determine the affinities of the metals for different acids by comparing the rates at which the metals liberate gas from acids of different concentration He found that if an acid of a given concentration dissolves one unit of metal per hour, an acid of half that concentration will take two hours to dissolve the same amount of metal The velocity of these reactions can be measured by finding the amount of

[1] Some try to evade the difficulty by using other terms "elective attraction," "chemical activity," "chemical avidity," "chemical energy," etc, but the original term, "chemical affinity," is convenient, provided it is kept in its place

[2] *si amor dicendus copulæ cupido*

gas liberated per minute, or the amount of acid or of metal consumed, say, every minute Then, at any given moment

$$\text{Velocity} = \frac{\text{Amount of gas liberated}}{\text{Time occupied}} = \frac{\text{Acid consumed}}{\text{Time occupied}}$$

The affinity of a metal for an acid depends on the concentration of the acid. In fine, the velocity of the chemical action at any instant is proportional to the concentration of the reacting substances

If we start with a solution of such a strength that it contains a gram molecules of acid per unit volume, then at the end of a certain time t, x gram-molecules of the acid per unit volume will have been consumed, and the solution will contain $a - x$ gram molecules of the acid per unit volume Hence, the velocity of the reaction will gradually slacken down At the beginning of the reaction, the velocity V will be proportional to a, that is, $V = ka$, where k is a constant,[1] and at the end of the time t, the velocity will be

$$\underline{V = k(a - x)}$$

Hence, in Wenzel's experiment, when $x = \frac{1}{2}a$, the reaction is only progressing half as fast as at the beginning when $x = 0$ The speed of the reaction at different times is illustrated in Fig 33, where the abscissa axis represents time, and the ordinate axis, the velocity expressed in any convenient units

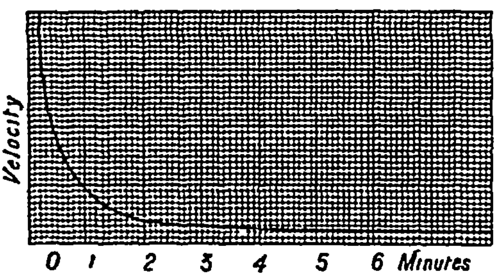


Fig 33—The Reduction in the Speed of Chemical Action with Time

By measuring the rate at which hydrogen is liberated per minute per unit area of the different metals on the same sample of dilute acid, it is possible to get a rough idea of the relative affinities of the different metals for that particular acid. Experiment shows that with dilute hydrochloric acid, starting with the most vigorous, this order is

Potassium, sodium, calcium, magnesium, zinc, and iron

By measuring the rates at which hydrogen is evolved with one metal and different acids of equivalent concentration, we get an idea of the relative affinity of the acids for the given metal[2] For instance, acids containing 36 5 grms of HCl (hydrochloric acid) per litre, 49 grms of H_2SO_4 (sulphuric acid), and 60 grms of CH_3COOH (acetic acid) per litre are chemically equivalent to one gram of hydrogen when tested by the methods indicated in Fig 32 When such acids react with magnesium ribbon

[1] Text books on algebra prove that when x is proportional to y $x = ky$, where k is a constant

[2] The dissolution of metals in acids is not suited for exact measurements because so many disturbing influences are at work—local rise of temperature, bubbles of gas protecting the surface of the metal from attack, variations in the surface of the metal during the action, etc Still, the conclusion indicated above is in harmony with a great deal of work on a variety of simple reactions.

(say, 0 05 grm) the relative affinities appear to be in the order named.

Hydrochloric acid	100
Sulphuric acid	70
Acetic acid	0 5

The first gives off most hydrogen in a given time, the latter least.

Returning to the law symbolized in the equation $V = k(a - x)$, with the acids of unit concentration, it follows that the velocity $V = k$ And k has accordingly been called the "affinity constant" of the acid for the metal, k represents the speed of the reaction at the instant when the acid has unit concentration The result of this discussion shows that the velocity of a chemical reaction is proportional (1) to the "affinity constant" between the reacting substances, and (2) to the concentration of the reacting substances

§ 6 Opposing Reactions Guldberg and Waage's Law.

In an aggregate of molecules of any compound, there is an exchange constantly going on between the elements which are contained in it —A W WILLIAMSON (1850)

Some of the earlier chemists—*e.g* Tobern Bergmann (1783)—argued that the result of a chemical change must be in favour of that substance with the stronger affinity Accordingly, "Affinity Tables" were compiled to show the order in which the different substances would displace one another from a given compound *If A displaces B from one compound, and B displaces C from another compound, the order of the affinity of these three substances is A, B, C* It was clearly recognized that this method of work does not give a numerical measure of affinity, but it was thought that relative results were obtained The suggestion is certainly a good trial hypothesis Let us compare it with the facts.

We have seen that iron can displace hydrogen from its combination with oxygen, hence iron has a stronger affinity than hydrogen for oxygen. Similarly, we have seen that hydrogen can displace iron from its combination with oxygen, consequently, hydrogen has a stronger affinity than iron for oxygen These two conclusions are contradictory, both cannot be true Therefore *the affinity hypothesis must be either false, or some powerful perturbing influence must be at work*

C L Berthollet clearly recognized an important disturbing factor in 1799 Berthollet noticed large quantities of "trona"—sodium carbonate —on the shores of the natron lakes of Egypt He suggested that the sodium chloride brought down by the rivers was decomposed by the calcium carbonate present on the banks of these lakes.

$$CaCO_3 + 2NaCl = CaCl_2 + Na_2CO_3$$

Berthollet knew, quite well, that this reaction is the reverse of that which usually obtains in the laboratory, for sodium carbonate, when added to calcium chloride, precipitates calcium carbonate

$$Na_2CO_3 + CaCl_2 = CaCO_3 + 2NaCl$$

But, added Berthollet, the large masses of calcium carbonate on the banks of these lakes is able to "strengthen" the weak affinity of carbon dioxide for sodium, or of chlorine for calcium Here Berthollet brings the disturbing factor into bold relief Chemical action is conditioned not only

by affinity but by the relative concentrations of the reacting bodies Excessive concentration can compensate for a weakness of affinity A chemical reaction can be reversed by changing the concentrations of the reacting bodies. We must apply Berthollet's hypothesis to the reaction under consideration—the action of iron on steam

At the outset, it will be obvious that we have to deal with two opposing reactions steam reacts with iron to produce iron oxide and hydrogen

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

and iron oxide and hydrogen react to produce steam and metallic iron

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O$$

Two independent and antagonistic changes take place simultaneously in the system The result of the change will be determined by the fleeter reaction When steam is passed over red-hot iron, the hydrogen does not get much chance, it is carried away into the gas jar before it has had time to set up the reverse change Similarly, when hydrogen is passed over red hot iron oxide, the steam does not get a chance for it is carried away from the reduced iron by the stream of hydrogen

In order to study the affinity relations between these different substances, they should be heated in closed vessels so that the products of the reaction are not whisked away from the seat of the reaction as soon as they are formed. The result is then very curious. It seems as if the reaction stops after a time. At any rate, if the temperature remains constant, no further change can be detected, however long the system be heated. In other words, the system assumes a state of equilibrium. Experiment shows that at 200°, the system is in equilibrium when the volume of the steam is to the volume of hydrogen nearly as 20 1 Otherwise expressed, for equilibrium at 200°

$$\frac{\text{Volume of hydrogen}}{\text{Volume of steam}} = \frac{1}{20}$$

If a mixture of one volume of hydrogen and twenty volumes of steam be passed over iron filings or over iron oxide at 200° no apparent change will occur, for the mixture, after passing through the tube at 200°, will have the same composition as when it entered if no secondary actions occur If more than this amount of hydrogen be present at 200°, some iron oxide will be reduced until the equilibrium ratio 1 0·05 obtains, and conversely, if less than this amount of hydrogen be present, iron oxide will be produced until the equilibrium ratio is obtained If the temperature be raised, the velocities of the two reactions are altered in such a way that at 440° the volume of steam will be to that of hydrogen nearly as 6 1, or as 1 0 17, and at 1500°, as 1 1 This means that if equal volumes of steam and hydrogen be passed over iron filings or iron oxide at 1500°, no change in the composition of the gaseous mixture will be perceptible.

Chemical equilibrium is dynamic, not static.—Let us now try to picture what is taking place Start with metallic iron and steam At the outset when the reaction is just starting, the velocity of decomposition of the steam will be greatest because the system then contains the greatest amount of reacting substance, and we have seen, p 96, that "the velocity of chemical action is proportional to the concentration of the substances taking part in the reaction" From this moment, the velocity of the reaction gradually slows down as the concentration of the reacting steam

becomes less and less On the other hand, the velocity of the reverse action will be zero at the commencement, because none of the reacting hydrogen is then present The speed of the reverse change will become faster and faster as the product of the first-named reaction—hydrogen—accumulates in the system Ultimately, a point will be reached where the velocities of the two opposing reactions will be equal The one will be balanced by the other The reaction will appear to have stopped in spite of the fact that more or less of the original substance still remains untransformed The system is then in a state of equilibrium No further change will occur, however long the substances be heated under the same physical conditions of temperature, etc Chemical changes of this kind are conveniently styled opposing or balanced reactions The idea of a dynamic and not a static equilibrium in such reactions was emphasized by A W. Williamson about 1850, while studying the action of acids on alcohol He said "an exchange is constantly going on between the elements of the molecules of a compound so that each atom of hydrogen in the molecules of HCl present in a drop of hydrochloric acid does not remain quietly in juxtaposition with the atom of chlorine with which it first united, but, on the contrary, is constantly changing places with the other atoms of hydrogen, or, what is the same thing, changing chlorine," and he further adds that when a system appears to be in equilibrium, that condition "is only kept up by the number of exchanges in one direction being *absolutely* the same in each moment of time as those in the opposite direction"

Reversed pointers "$\rightleftharpoons$" are conventionally used in place of the symbol "$=$" for opposing reactions, so as to indicate that two reactions are proceeding simultaneously "from right to left" and "from left to right" Accordingly, the reaction under consideration is symbolized

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

Opposing reactions are also called incomplete or reversible reactions in contradistinction to irreversible or complete reactions typified by the action of zinc on sulphuric acid, where the reaction is completed in one direction and is not opposed by a counter reaction

It is not difficult to see that the *absolute quantities* of steam, hydrogen, iron, and iron oxide, in the reaction under consideration, do not matter The velocities of the two opposing reactions, and therefore the distribution of the reacting substances, when in equilibrium, is determined by the relative concentrations of the changing substances This is conveniently expressed by the number of gram-molecules of each present in unit volume Thus 18 grams of water—H_2O—per litre represents one gram-molecule, 36 grams of water per litre, two gram-molecules, etc. The concentration of a reacting substance is sometimes (inappropriately) called its active mass, Berthollet called it chemical mass.

If the surface of the iron were doubled, it is true that twice as many molecules of the black oxide, Fe_3O_4, might be formed in a given time by the decomposition of the steam, but then twice as many molecules of Fe_3O_4 would be decomposed by the hydrogen in the same time Hence, the amount or the concentration of the solid can have no appreciable influence on the equilibrium, although it may affect the speed at which the state of equilibrium is attained In studying equilibria in

gases and liquids, anything which separates in the solid condition is often supposed to be thrown out of the reacting system because the state of equilibrium is independent of the concentration of the solid, and a liquid which separates when studying gaseous equilibria, is also supposed to be thrown out of the reacting system We shall find an analogy in studying the vapour pressure of water in presence of its own liquid The vapour pressure is independent of the *amount* of liquid water present

The decomposition and formation of mercuric oxide at different temperatures (p 10) in a closed vessel is another example of opposing reactions, because the two reactions proceed simultaneously $2HgO \rightleftharpoons 2Hg + O_2$

Steam alone is decomposed when heated to a high temperature The higher the temperature the greater the amount decomposed, or dissociated into its elements $2H_2O \rightleftharpoons 2H_2 + O_2$ For instance, W Nernst and H. von Wartenberg (1906) found

Temperature	1000°	1500°	2000°	2500°
Amount dissociated	0 00003	0 0221	0 5880	3 98 per cent

This means that if 100 grms of steam be heated to 2500°, at atmospheric pressure, the mixture will be in equilibrium when it contains approximately 96 grms of steam, 3 55 grms. of free oxygen, and 0 45 grm of free hydrogen If the temperature be lowered some of the hydrogen and oxygen will recombine, if the temperature be raised more steam will be decomposed. When a substance decomposes with a change in the physical conditions—temperature, pressure, etc —and the products of decomposition recombine when the original conditions are restored, the process of decomposition is said to be dissociation

The ideas developed in this section were not so clear to the old workers, not even to Berthollet himself, for Berthollet appears to have confused the incompleteness of certain reactions with the law of multiple proportions The confusion gave him some strong arguments in the "Berthollet *v* Proust Controversy," indicated on p 15 Proust did not know enough to clarify Berthollet's argument.

Chemical affinity —To summarize the preceding discussion chemical affinity is a convenient term for the driving force which causes certain substances to combine together and to remain united with one another

1 The force seems to act only when the reacting substances are in contact with one another, or, as it is sometimes expressed "when the substances are brought within 'insensible' distances of each other"
2 It is a selective force and it seems to act more intensely the more unlike the substances are, or, as it is sometimes expressed "like reacts with the unlike"
3 The affinity of an element is not only definite as to *kind*, but it is also definite as to the *quantity* of the elements which enter into combination The quantitative characteristics are described by the "Laws of chemical combination," discussed in Chapter II
4. The strength of the affinity varies with changes in the conditions of temperature, pressure, light, etc
5 The velocity of the effect produced by chemical affinity is modified by the relative concentrations—active masses—of the reacting substances.

The principles of opposing reactions just outlined are included in Guldberg and Waage's law of mass action so called because the ideas of Berthollet were considerably extended by C M Guldberg and P. Waage in an important memoir published in 1864

§ 7 The Properties of Hydrogen.

The more salient properties of hydrogen have been discussed on p 44 Hydrogen is not very soluble in water—100 volumes of water at 0° absorb about 2 volumes of gas, and at 20°, 1 8 volumes of gas Hydrogen was once used as the standard for the atomic weights because it is the lightest element known. The lightness of hydrogen has been illustrated, Fig 10, p 43 A cardboard box or a light glass vessel can be counterpoised, bottom upwards, on a balance The beam will ascend when hydrogen is poured upwards into the inverted vessel Soap-bubbles blown with the gas, or collodion balloons filled with the gas, rise to the ceiling very quickly Hydrogen is accordingly used for filling balloons Coal gas is used for the same purpose, it is much cheaper than hydrogen, though not quite so buoyant

Hydrogen is not poisonous, and animals placed in hydrogen are suffocated for the want of oxygen When hydrogen is inhaled, the voice becomes shrill—approaching falsetto The pitch of organ pipes and other wind instruments is raised if a blast of hydrogen be used in place of air

Just below the critical temperature, $-241°$, a pressure of about 20 atmospheres will liquefy the gas, above the critical temperature, no pressure, however great, will liquefy the gas This is one definition of "critical temperature" The liquid is clear and colourless, resembling water, but it has a specific gravity 0·07, and boils at $-252°$ Hydrogen solidifies when the liquid is evaporated in a partial vacuum. The white solid is crystalline, melts at $-259°$, and has a specific gravity 0 076. The data concerning the change of state of hydrogen can be symbolized

$$\text{Hydrogen}_{\text{solid}} \overset{-259°}{\rightleftharpoons} \text{Hydrogen}_{\text{liquid}} \overset{-252°}{\rightleftharpoons} \text{Hydrogen}_{\text{gas}}$$

The combustible qualities of hydrogen have been indicated on p 44 The oxyhydrogen flame is one of the hottest gas flames known When a stick of quicklime is placed at the tip of the flame from a mixture of hydrogen and oxygen burning from a special jet to avoid risk of explosion, the lime does not melt, but it becomes white hot and glows with an intense white light known as "Drummond's light," or the "lime-light" or "calcium light" If zirconia be used in place of lime, the "zircon light" is obtained The oxyhydrogen flame is also used for welding, soldering platinum, etc

Catalytic agents.—Although the combustibility of hydrogen is one of its most characteristic properties, perfectly dry hydrogen ignites with difficulty, if at all, when mixed with perfectly dry oxygen Note, however, that "moisture" is a product of the reaction Many other combustible substances, if perfectly dried, do not burn when moisture is rigorously excluded The moisture is here said to act as a catalytic agent—κατὰ (kata), down, λύω (lyo), I loosen Finely divided platinum is also a catalytic agent for a mixture of hydrogen and oxygen, for, in

contact with freshly ignited finely divided platinum, or platinized asbestos,[1] these gases can combine at much lower temperatures than they can do in its absence The platinum suffers no perceptible change during the action

Hydrogen and oxygen, so far as we can tell, may remain an indefinite time in contact with one another at atmospheric temperatures without showing any sign of chemical action Some say that the gases do react, but very very slowly By measuring the diminution in the speed of the reaction from, say, 600° to 500° to 400° to 300°, and assuming that the rate of diminution of the speed of the reaction follows that same law—reduction of the speed one half per 10° reduction of temperature—it has been stated that no appreciable amount of hydrogen and oxygen will have combined if a mixture of these gases be allowed to stand at ordinary temperatures 1,000000,000000 years The student has the option of accepting or rejecting statements like these They can neither be proved nor disproved. As P Duhem has said (1910) "It comes to the same thing experimentally whether we say that the velocity of a reaction is absolutely null, or that it is so small that there is no way of detecting it"

Returning to the catalytic agent—finely divided platinum If a jet of hydrogen be allowed to impinge on recently ignited but cold platinized asbestos, the mass of platinum becomes hotter and hotter until finally the temperature is sufficient to ignite the hydrogen gas Similarly, if fresh platinized asbestos be placed in a mixture of hydrogen and oxygen, the gaseous mixture will explode in a short time The platinum is said to act, not by starting the reaction, but simply by accelerating the immeasurably small speed of combination of the cold gases until they combine at a prodigious rate The student of chemistry must bear in mind that this is the fashionable view of the function of the catalytic reagent, to morrow it may be unfashionable We do not really know how the catalytic agents—moisture and platinized asbestos—act. "Toy" automatic cigar lighters are made so that by turning the tap of a little hydrogen generator—not unlike the Kipp's apparatus in principle—a jet of hydrogen can be directed on to a piece of spongy platinum when a "light" is desired. The platinum becomes hotter and hotter, and finally ignites the jet of hydrogen The flame is extinguished by turning the stopcock, and the apparatus is ready for another ignition when the jet of hydrogen is again turned on to the platinum This is the principle of the self lighting lamp designed by J W Döbereiner in 1822 Impurities in the hydrogen gas, however, appear to "poison" the platinum, for the apparatus soon ceases to be effective

§ 8 The Action of Hydrogen on the Metals

Absorption or occlusion —Some metals—particularly platinum and palladium—absorb relatively large volumes of hydrogen According to Thomas Graham (1867–9), palladium will absorb 935 times its own volume of hydrogen in cooling from a red heat, and at ordinary temperatures, 276 times its volume The actual amount absorbed depends upon the physical condition of the metal According to G Neumann and F Streintz

[1] Asbestos is dipped in a solution of platinum chloride and ignited A deposit of very finely divided platinum is left on the asbestos, which is then called *platinized asbestos*

(1892), one volume of the following finely divided metals will absorb the following volumes of hydrogen —

Palladium black	502 3	Nickel	15 6
Platinum sponge	49 3	Copper	4 5
Gold	46 3	Aluminium	2 7
Iron	19 2	Lead	0 1

The hydrogen is given off when the metal is heated, particularly under reduced pressure, and this property of palladium furnishes a useful means of weighing hydrogen gas It was used by Morley in his work on the combining weights of oxygen and hydrogen (p 46)

Palladium increases in volume during the absorption, but its general appearance and properties are not much altered, although a considerable amount of heat is evolved during the absorption Graham called the phenomenon occlusion (from *occludo*, I shut up) The gas is said to be occluded by the metal The phenomenon is now generally called adsorption, meaning that the gas *ad*heres in some unknown way to the metal It was once thought that the palladium formed a chemical compound—Pd_2H—with the hydrogen, but this has not been accepted as a full explanation Graham thought that the gas hydrogen condensed to a solid, and behaved as if it formed an alloy with the palladium He gave the name hydrogenium to this hypothetical solid to indicate its supposed metallic nature Solid hydrogen, however, has rather the properties of a non-metal, not a metal—its specific gravity, for instance, is but one eighth that calculated for adsorbed hydrogen in palladium The relation between the adsorbed hydrogen and the metal is not quite clear

Nascent state —Hydrogen at the moment of its formation is more chemically active than ordinary hydrogen For instance, ordinary hydrogen can be passed into an acidified solution of ferric chloride without producing any appreciable change, but if metallic zinc be placed in the solution, the brisk evolution of hydrogen is soon attended with the reduction of the ferric chloride to ferrous chloride The latter gives no reddish coloration with a solution of potassium thiocyanate, the former gives a blood-red coloration Hence, hydrogen in the *nascent condition—in statu nascendi*—can do chemical work which the ordinary gas cannot do "Hydrogenized palladium" also can do chemical work which ordinary gaseous hydrogen cannot do It can reduce a solution of ferric chloride to ferrous chloride, for instance —

$$FeCl_3 + H_{palladium} = FeCl_2 + HCl$$

We shall find later on that at least three possible hypotheses are available for explaining this phenomenon !

Permeability of the metals to gases —Hydrogen gas can diffuse through solid platinum, palladium, iron, etc For instance, if hydrogen be passed through a palladium tube, the gas escapes comparatively quickly through the walls of the metal It has been estimated that about 4 litres of hydrogen can pass through a square metre of palladium per minute, and about half a litre through a square metre of platinum in the same time [1] The explanation of this action is probably connected with the adsorption of the gas by the metal This phenomenon has to be taken into consideration in chemical analysis when certain substances are heated over the gas

[1] About 130 c c of hydrogen will diffuse through a sheet of indiarubber about the same size and thickness in the same time.

flame in a platinum crucible Reducing gases, from the coal gas, pass through the walls of the crucible and exert a reducing action on substances being calcined—*e g* manganese oxide

Hydrides —Hydrogen forms compounds with most of the non metals and many of the metals. These compounds are called hydrides Hydrides of the non metals are usually stable, while the hydrides of the metals are relatively unstable Not only is water an oxide of hydrogen, but it can also be regarded as an oxygen hydride Ammonia—NH_3—is a nitrogen trihydride, hydrazoic acid—N_3H—is a trinitrogen monohydride, methane—CH_4—and the hydrocarbons generally are carbon hydrides. Arsenic hydride—AsH_3, phosphorus hydride—PH_3 etc, are examples of non metallic hydrides, while potassium hydride—KH, sodium hydride—NaH,[1] etc, are examples of metallic hydrides Calcium hydride—CaH_2—is sold under the name "hydrolith" for making hydrogen By simply treating hydrolith with water, hydrogen is evolved

§ 9 The Diffusion of Gases

Owing to the fact that air is 14 times as heavy as an equal volume of hydrogen under the same physical conditions, if a jar of hydrogen be placed mouth upwards under a jar of air, mouth downwards, most of the hydrogen will flow upwards into the upper cylinder, and air will flow downwards into the lower cylinder—Fig 34 The action is analogous with what would occur if the lower cylinder contained an oil and the upper cylinder water The oil and water would change places The two liquids can be left an indefinite time without mixing, for the two liquids—oil and water—are immiscible On the contrary, the two gases—hydrogen and air—will spread throughout the two vessels in a short time and in such a way that the two cylinders will enclose a homogeneous mixture of air and hydrogen The gases are miscible in all proportions Had the two liquids been soluble in one another—say alcohol and water instead of oil and water—these also would have diffused one into the other so as to form a homogeneous solution of alcohol and water

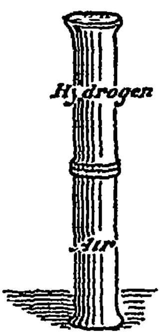


FIG 34 — Diffusion Experiment

The process of diffusion in the case of liquids appears to be very much slower than with gases The molecules of gases seem to lead a more or less independent existence This is illustrated by the rapidity with which the molecules of, say, ammonia can travel from one end of a room to the other and affect the sense of smell In liquids, however, the molecules are much less mobile This can easily be proved by dropping a small grain of aniline dye into a tumbler of clear still water The water will be uniformly coloured in a few weeks. The molecules of solid substances have practically lost their mobility But not all Carbon laid in contact with pure, hot, solid iron will diffuse into the mass of the metal, gold in contact with lead will in a few years, diffuse into the lead in appreciable quantities, carbon will diffuse into the body of hot vitrified porcelain, and metallic silver will diffuse into hot glass, staining it yellow

[1] The formulæ Na_2H and K_2H, given by L Troost and P Hautefeuille (1873), are considered to be erroneous

The transfer of gases in bulk from one vessel to another is an effect of gravitation, whereas diffusion is not an effect of gravitation. Thomas Graham (1832) showed that the speed at which the molecules of a gas can diffuse or travel through thin porous membranes is related to the specific gravity of the gas. For example, hydrogen diffuses nearly four times as fast as oxygen; the relative densities of hydrogen and oxygen are nearly as 1 : 16, and the relative rates of diffusion of the two gases are nearly as $\sqrt{16} : \sqrt{1}$, *i.e.* as 4 : 1. Thus we have Graham's law of diffusion: **the relative speeds of diffusion of gases are inversely proportional to the square roots of their relative densities.** Graham measured the speed of diffusion of gases through thin porous plates, and found the numbers indicated in the last column of the subjoined table.[1] The preceding column represents the theoretical numbers calculated on the assumption that the speeds of diffusion are inversely as the relative densities. The observed numbers for the speeds of diffusion agree very closely with those obtained by calculation. There is an interesting application of the law.

TABLE VI.—SPEEDS OF DIFFUSION OF SOME GASES AND GRAHAM'S LAW.

Gas	Relative density H = 1	Calculated speed of diffusion (from $\frac{1}{\sqrt{\text{relative density}}}$)	Observed speed of diffusion (Hydrogen = 1)
Hydrogen	1	1	1
Methane CH_4	8	0.354	0.351
Carbon monoxide (CO)	14	0.267	0.278
Nitrogen	14	0.267	0.265
Oxygen	16	0.250	0.248
Carbon dioxide (CO_2)	22	0.213	0.212

To find the relative density of a gas by comparing its speed of diffusion with that of another gas of known density.—Let D_1 and D_2 represent the relative densities of two gases one of which, D_1, is known, the other, D_2, is unknown. Suppose that the relative speeds of diffusion of the two gases V_1 and V_2 are known. Then, it follows from Graham's law:—

$$V_1\sqrt{D_1} = V_2\sqrt{D_2}$$

Given any three of these numbers, the fourth can be calculated by arithmetic.

EXAMPLES.—(1) The speeds of diffusion of carbon dioxide and of ozone were found by Soret (1868) to be as 0.29 (V_1) is to 0.271 (V_2). The relative density of carbon dioxide is 22 (D_1) when H = 1. What is the relative density of ozone (D_2)? From the preceding relation, it follows that $\sqrt{D_2} = 0.29 \times \sqrt{22} \div 0.271 = 0.29 \times 4.69 \times 3.69$; or $D_2 = (5.02)^2 = 25$ nearly.

(2) A. Ladenberg (1898) found that ozonized air required 367.4 seconds to diffuse under conditions where pure oxygen required 430 seconds: what is the specific gravity of the ozonized air, assuming that the specific gravity of oxygen is unity? Ansr. 1.3689.

[1] I have recalculated Graham's numbers to H = 1 instead of air = 1; I have also used whole number approximations for the relative densities.

Advantage has been taken of the different speeds of diffusion of different gases to devise several pleasing experiments The simple facts can be illustrated by fixing porous pots [1] to the ends of bent tubes as shown in the Figs. 35–37 The porous pots contain air Bring a cylinder of hydrogen over the one porous pot, Fig 35 Hydrogen diffuses through the walls of the pot faster than the air can diffuse outwards Consequently, the pressure of the gas inside the porous pot will increase This is shown by the motion of the coloured liquid in the U-tube away from the porous pot. Before the cylinder of hydrogen was placed over the porous pot, the air diffused inwards and outwards through the pot at the same rate. Repeating the experiment, Fig 36, with a cylinder of carbon dioxide instead of hydrogen, the air moves outwards from the porous pot faster than the carbon dioxide can pass inwards. Consequently, there is a reduction in the pressure of the gases in the porous pot. This is shown by the motion of the liquid in the U-tube towards the porous pot.

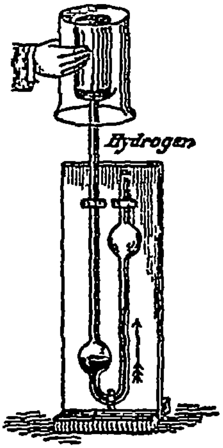


FIG 35

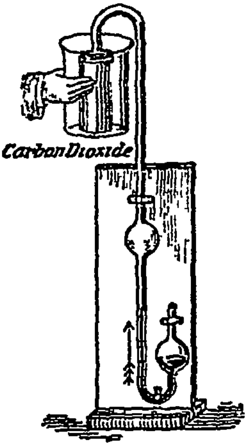


FIG 36

Diffusion Experiments

If the liquid in the leg of the U-tube be connected with a battery and electric bell, and if a wire be fused in the leg of the U-tube so that when the liquid rises electric contact is made, the bell will ring A device based on this principle has been suggested as an alarm indicator for the escape of coal gas in rooms, or fire damp in coal mines. These gases, like hydrogen, diffuse through the walls of porous pots faster than the air can escape The experiments, Fig 35, can be modified so that the liquid is sprayed from the tube like a miniature fountain. The outward pressure of the gas, Fig 35, can be made to blow a soap bubble if a film of soap solution be placed across the widened mouth of the tube, Fig 37

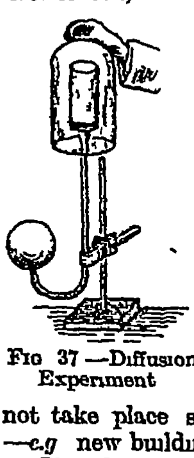


FIG 37 —Diffusion Experiment

The ready diffusion of gas through the walls of buildings plays a part in ventilation. Most building materials are porous, and permit the passage of gases through them in both directions. The diffusion does not take place so readily when the walls are saturated with moisture —*e.g* new buildings, etc

If a slow current of electrolytic gas, that is, the mixture of hydrogen

[1] Generally used for battery cells Ordinary clay tobacco pipes with the mouth of the bowl closed with plaster of Paris will serve quite well for the experiment

and oxygen obtained by the electrolysis of water, be allowed to pass through the stem of a "church-warden" clay pipe, and the gas issuing from the pipe be collected in a gas trough, the gas thus collected will no longer explode when brought in contact with a flame. On the contrary, it will rekindle a glowing chip of wood, showing that oxygen is present. In passing through the porous pipe, hydrogen escapes by diffusion through the porous walls of the "clay tube" much more rapidly than the heavier oxygen. This phenomenon—the separation of one gas from another by diffusion—has been called, by Graham, atmolysis—ἀτμος (atmos), vapour, λύω (lyo), I loosen. If a current of steam be passed through a porous tube at a high temperature, and if the porous tube be surrounded by another tube of glazed impervious porcelain, the water vapour will be dissociated by the heat into hydrogen and oxygen, p. 100; since the hydrogen diffuses much faster than the oxygen, hydrogen will pass from the inner tube into the annular space between the two tubes. The hydrogen may be collected in a suitable gas trough. Similarly, the residual oxygen can be collected from the gaseous steam passing along the inner tube. Of course, the hydrogen is contaminated with more or less oxygen, and the oxygen with more or less hydrogen.

Are the molecules of a gas all alike?—Experiments on atmolysis enable an answer to be returned to this question. If a gas like hydrogen or oxygen be allowed to diffuse through a porous septum, no difference can be detected in the properties of the gas on both sides of the septum. If some of the molecules of, say, hydrogen had a sensibly greater density than the others, it would be possible to produce two kinds of hydrogen by atmolysis. This cannot be done, and hence it is inferred that if there is a difference in the molecules of hydrogen, it is too small to be detected. The alternative is that if there is a definite proportion of two kinds of molecules in equilibrium, equilibrium is restored on both sides of the septum as soon as the two kinds of molecules are separated. W. Ramsay and J. N. Collie (1897) inferred that helium is a simple substance because repeated atmolysis does not alter its density; and Lord Rayleigh and W. Ramsay (1895) showed that atmospheric nitrogen is probably a physical mixture of nitrogen with a heavier gas, because repeated atmolysis does alter its density.

Questions

1. Indicate by means of equations four methods of preparing hydrogen. What weight of zinc is required to produce 100 litres of hydrogen gas measured at 27° C. and 680 mm. pressure? (Zn = 65. 22.4 litres of oxygen measured at 0° and 760 mm. weigh 32 grams.)—*St. Andrews Univ.*

2. Explain the connection between the terms Equivalent and Atomic weight. 0·100 gram of a metal gave on treatment with a dilute acid 34.2 c.c. of hydrogen measured at N.T.P. Calculate the equivalent of the metal. What further information is required in order to deduce the atomic weight?—*Aberystwyth Univ.*

3. What is meant by "atmolysis"? The specific gravities of air and hydrogen are as 1 : $\frac{1}{14.4}$. How many cubic centimetres of hydrogen will pass through a stucco plug in the same time that 1 c.c. of air will pass through?—*Science and Art Dept.*

4. When 2.331 grams of lead oxide are heated in hydrogen, 2.163 grams of metallic lead are obtained. Suppose the atomic weight of oxygen to be 16, find the quantity of lead combined with 16 parts of oxygen.—*Oxford Senior Locals.*

5. Ten grams of water are (1) decomposed by sodium; (2) passed as steam over red hot iron; (3) decomposed by an electric current. What volume of gas under standard conditions is produced in each case?—*Owens Coll.*

CHAPTER VII

THE KINETIC THEORY OF ATOMS AND MOLECULES

§ 1 Matter and Energy

Substance is like a river in continual flow the energies undergo constant changes and cause work in infinite variety There is hardly anything that stands still or remains still.—MARCUS AURELIUS

MATTER as perceived by the senses, possesses certain attributes—weight and extension in space—which *appear* to be permanent and essential qualities abiding in *all* known kinds of matter, whereas other properties appear to be secondary and accidental attributes—*e g* colour, odour, etc which are peculiar to *specific* forms of matter Matter may also be found under different conditions of temperature, electrification, motion, etc, and daily experience teaches us that changes are continually taking place in the conditions of bodies around us Change of position, change of motion, of temperature, volume, and chemical combination are but a few of the myriad changes associated with bodies in general.

The forms of energy —It is evident that, in order to keep a grindstone in motion, a certain amount of, say, muscular energy must be expended to overcome the resistance opposed by the air, axle bearings etc. If a piece of steel be pressed against the stone, the steel soon becomes warm. Exact measurements have shown that the amount of heat produced is proportional to the energy expended in maintaining the motion of the grindstone Again, in the hot-air motor, heat is employed to set bodies in motion. Heat and mechanical motion are therefore mutually convertible, one into the other If a vulcanite tire be placed on the grindstone, and the rim be pressed with a piece of flannel, electrification will be induced. But electricity can also be readily re converted back into mechanical motion. Electricity, mechanical motion, and heat are thus mutually convertible one into the other Much of the motive power used in the industrial arts is derived from the chemical action between coal and oxygen in the furnace of a steam engine. Heat and electricity are also well-known concomitants of chemical action Hence we infer that heat, electricity, mechanical motion, and chemical action are all different forms of one distinct entity—energy Observations by Joule and others have shown that any one form of energy can be transformed directly, or by intermediate steps, into any other form This is the so called law of transformation of energy All types of machinery are devices for transforming energy from one form into another

Energy and work.—As a first approximation, every change in the condition of the bodies around us is supposed to be due to the action of

energy In other words, energy is that which has the power of changing the conditions of bodies Whenever a body is changing its condition, there energy is in action Energy is the cause, change of condition the effect The action of energy may be resisted Change can only take place when the restraint is withdrawn or overcome The action by which energy produces a tendency to change is called a *force* The word "tendency" here means that the change will take place the moment the restraining influence is withdrawn Force is thus a manifestation of energy. Whenever resistance is overcome, energy must be expended Hence energy is sometimes defined as "the power to overcome resistance" Work is said to be performed whenever change takes place in opposition to a force opposing that change The amount of work done is equal to the quantity of energy transferred Work is done at the expense of energy.

$$\text{Work performed} = \text{Energy expended}$$

Consequently, energy is sometimes defined as "the capacity for doing work," or, as W Ostwald puts it, energy is work and all else that can be produced from and be converted into work Two factors are therefore involved in the expenditure of energy (1) the *magnitude* of the resistance, and (2) the *extent* to which the resistance is overcome Thus, when a particle moves a certain distance s by the application of a force F, the amount of energy expended, or the work done, is equal to the product Fs

Energy and matter are inseparable—We can conveniently describe our knowledge of the material world in terms of two[1] entities or abstractions 1 Energy, 2 Matter It is sometimes convenient to keep these two concepts distinct, although energy and matter are separable only in thought, in reality they are indissolubly joined together We leave the *metaphysical*[2] chemist to deal with matter defined as the unknown cause of known sensations, and answer for himself such questions as What is matter in and by itself? What is the "*Ding an sich*"?[3] The *working* chemist defines **Matter is that which possesses weight[4] and occupies space[5]** Air, water, glass, copper, etc, are forms of matter, heat, light, electricity, and magnetism are forms of non-matter—energy, colour, odour, etc, are specific properties of particular forms of matter

Energy, like matter, is indestructible—So far as accurate measurements are concerned, it is found that when any quantity of one form of energy is made to disappear, an equivalent quantity of another form or

[1] In studying light, etc, it is convenient to add a third—the æther—the hypothetical medium through which the rays of light, etc, are propagated

[2] By "metaphysics," I here understand with A Schopenhauer (*Welt als Wille und Vorstellung*, Berlin, 2, 180, 1854), "every pretended cognition which goes beyond experience, and therefore beyond nature in order to give information about that upon which nature is dependent, popularly expressed, what is behind nature, and makes nature possible"

[3] German—"the thing in itself" At the end of our discussion, too, the student might have the uncomfortable feeling that his time had been spent poking into nothing

[4] See the last footnote p 7

[5] W Ostwald (1892) "The more intimately acquainted I became with the properties of energy, the clearer became the proof that matter is nothing but a complex of different factors of energy which possess the property of being reciprocally proportional The traditional fundamental properties of matter show themselves as modes of expression or factors of energy"

forms of energy appears. No gain or loss of energy has ever been observed in an isolated system. This is the famous law of conservation or persistence of energy. "The transactions of the material universe," said J. C. Maxwell, in that inimitable work *Matter and Motion*, "appear to be conducted, as it were, on a system of credit. Each transaction consists of a transfer of so much credit or energy from one body to another. The act of transfer or payment we call work."

Perpetual motion.—The law of persistence of energy is sometimes called the first law of thermodynamics. It can be expressed another way: No machine can generate energy or do work of itself without consuming at least an equal quantity of "pre-existing" energy. We call this revised statement of the law of persistence of energy, the law of excluded perpetual motion. We can offer no proof of the truth of this law, other than the uncontradicted experience of mankind. We assume that if perpetual motion had been possible it would have been discovered long ago. Of course a similar argument might have been used in 1890 against the existence of a gas like argon in the atmosphere, and the "uncontradicted experience" would have been contradicted four years later. The search for a perpetual motion through centuries of laborious work has been fruitless. It has brought nothing but failure. So great is our faith in the truth of this unproved "law" that a demonstration showing that any supposed process would involve a perpetual motion, *i.e.* the creation or destruction of energy, is considered sufficient proof that the supposed process is impossible. Most scientific societies would refuse to consider seriously papers which violated the assumed law of excluded perpetual motion.

§ 2. Total, Available, and Potential Energy.

We have no means of measuring the absolute or *total* amount of energy which a body possesses. Air confined in a closed vessel at atmospheric pressure might appear to possess no energy because it can do no work. But reduce the pressure of the surrounding air, and the air confined in the vessel is capable of performing work. The total energy associated with any body is possibly independent of the external conditions. In the study of natural phenomena, we are only concerned with that portion of the total energy which can be utilized for doing work. This is called the free or available energy.

Potential and kinetic energy.—There is an important difference between a stone lying on the ground, and a similar stone lying on the table. Both appear alike to be motionless, yet the latter possesses more available energy than the former. For example, the stone, in descending to the ground, could be made to transfer its energy to the mechanism of a clock, and do work. The available energy would thus be transformed into mechanical motion. For the same reason, a wound watch spring possesses more available energy than a similar spring not wound up. Thus, available energy may be active (*i.e.* kinetic) or passive (*i.e.* latent or potential).

When a marble is rolling along the ground, it has the power, in virtue of that motion, to change the state of another marble with which it might collide. A body, therefore, might possess energy in virtue of its motion. This energy is said to be in a *kinetic* or active condition. It is found that

the available kinetic energy K of a body of mass m moving with a velocity V, is $K = \frac{1}{2}mV^2$. This energy may be transformed into heat when the motion of the body is arrested Potential energy, on the other hand, is said to be "potential to" or "possible to" a body in virtue of its condition with respect to surrounding objects When a stone is lifted above the ground, the energy expended and the work done depend upon the weight w of the stone and the height h to which the stone is lifted. Consequently, the available potential energy E of the raised stone will be $E = wh$ The meaning is that a measurable quantity of energy is "stored up" or "rendered passive" in some way, and that this same amount of energy can be recovered [1] For instance, when the stone returns to the ground, it will, in falling, acquire an equivalent amount of kinetic energy. Again, water in an elevated position can do work in virtue of the law that "all liquids will flow to the lowest level that circumstances will permit" Consequently, water at the top of a hill possesses potential energy. A bent spring, a raised hammer, compressed air, and a piece of iron in the vicinity of a magnet, all possess potential energy Substances which in virtue of their relative condition, or the motions of their molecules, are capable of entering into chemical actions, are also said to possess potential energy Such is gunpowder, a mixture of metallic zinc and sulphuric acid, etc The light, heat, sound, and mechanical motion which attend the explosion of guncotton are equivalent to the chemical energy stored in the explosive

§ 3 The Degradation or Dissipation of Energy

The transformations of energy —Water may be transported from the top of a mountain to the valley beneath in a variety of ways · it may come down in underground channels, rivers, and rain , or in the form of snow, glaciers, or an avalanche So may energy pass from a state of high to a state of low potential in many and various ways, giving rise to mechanical, thermal, actinic, chemical, electrical, or magnetic phenomena In reality, the so-called "different forms of energy" correspond with the tendencies which any given system may have to change in particular directions If there is a tendency for the different parts of a system to come into closer contact, we have gravitation and cohesion , if there is a tendency to an equalization of temperature, thermal energy , and when there is a tendency to undergo transformation into another substance, chemical energy Hence the definition a chemical reaction is one mode by which energy can be transferred from one state to another We have seen many examples of the liberation of energy—heat, light, electricity—during chemical reactions To avoid the assumption that this energy comes from nothing, it is postulated that the original system contained a definite amount of available energy—chemical energy.

If a substance can unite with another, it is said to possess chemical energy, because it can do chemical work, and conversely, substances which cannot combine chemically with other substances have no available chemical energy, for they can do no chemical work. During a chemical

[1] Note that kinetic and potential energy are here referred to the earth as constant The suspended stone would have no available energy if it could never fall

reaction, the chemical energy is transformed into an equivalent amount of some other form of energy which is usually, though not always, heat (see p 20) Hence, the relation between chemical energy and heat (thermal energy) is an important subject, which, for convenience, is called thermo-chemistry Chemical energy may also be transformed into electrical energy during a chemical reaction That branch of chemistry which deals with the relation between chemical energy and electricity (electrical energy) is called electro-chemistry Just as chemical changes which are accompanied by an evolution of heat are called "exo thermal reactions," so reactions which are accompanied by an evolution of electrical energy have been called "exo electrical reactions," and conversely for "endo thermal" and "endo electrical" reactions

The degradation of energy—Just as water will always run down from a high to the lowest level that circumstances will permit, so in all processes with which we are acquainted, every known form of energy at a high potential always runs down to energy at the lowest potential circumstances will permit, and one of the most interesting facts in connection with all natural changes is this constant running down or degradation of energy Energy becomes less available for doing work. Every change which takes place in nature does so at the cost of a certain amount of available energy When we inquire whether or not a transformation can take place, the question to be answered is Will the occurrence involve the degradation of energy? If not, the transformation will not take place under the given conditions. An ancient philosopher has said that "all things are in motion," and we might add that that motion always involves the degradation of energy The transformation of energy in a given system only ceases when the available energy has run down to the level of its surroundings. The system is then said to be in a state of stable equilibrium.

Metastable equilibrium—We are, however, very familiar with systems in which the energy has not run down to the level of its surroundings and yet everything appears to be a state of stable equilibrium But the stability is only apparent. As a matter of fact, available energy does not always, *of itself*, run down to the level of its surroundings. For some unknown reason, an influence—conveniently called hysteresis or passive resistance (p 79)—prevents the initiation of the process of degradation of energy—a preliminary impulse is needed to start the process of degradation of energy "Passive resistance" is here used as a grouping or classification term. It explains nothing Just as the throttle valve of a steam engine must be moved before the engine can start on its journey, so may a preliminary impulse be required to set the process of degradation of energy in motion The flapping of an eagle's wing may suffice to start an avalanche rolling down the mountain side, with gunpowder the "preliminary impulse" may take the form of heat, with a mixture of hydrogen and oxygen, an electric spark, or the mere presence of spongy platinum, with a mixture of hydrogen and chlorine, a flash of light, or the addition of a piece of charcoal, with fulminate of mercury, a sudden shock, while the addition of a minute crystal will start the process of crystallization of a supercooled solution of sodium thiosulphate We may thus have a state of metastable, apparent, or false equilibrium, as well as a state of true or stable equilibrium We naturally inquire Is there any test

to distinguish between states of real and states of apparent equilibrium? We know that if a gas is in equilibrium with regard to volume and pressure it will satisfy the conditions of Boyle's law, volume and temperature, Charles' law, etc. But we have not always such useful tests at our disposal.

§ 4 The Molecular Theory of Matter.

> If we would become imbued with the spirit of the new philosophy of chemistry, we must begin by believing in molecules.—J. P. COOKE.

For purely chemical reasons, which culminated in Avogadro's hypothesis, we have seen how chemists have been led to invest matter with an imaginary structure which explains, very well, the various transformations which matter undergoes. Matter is supposed to be made up of extremely small discrete particles called molecules. **Molecules are the imaginary units which make up matter en masse.** Molecules are made up of one or more atoms. **Atoms are the imaginary units which make up the molecules.**

Molecular structure of matter.—Matter must be either a discrete or a continuous medium. Our study of diffusion in solids, liquids, and gases leads us to reject the hypothesis that matter is continuous, for how can two continuous media occupy the same space at the same time? Our study of the compressibility of gases—Boyle's law—leads to the same view. How can a continuous medium on rarefaction (that is, diminution of pressure) expand indefinitely? How can compression diminish the volume of matter itself? If matter be discrete, we can readily answer these queries. Compression involves a closer packing or a crowding together of the molecules by diminishing the space between them. This very explanation was given by Hero of Alexandria 177 B.C. ("There are void spaces between the particles of air just as there is air between particles of sand; when the air is compressed, the particles are forced into the vacant spaces, and when the pressure is removed they return to their former position.") Conversely, rarefaction involves an increase of the space between the molecules, so that the molecules become less closely packed and less crowded together. If matter be discrete we can also understand how one substance can diffuse into another—hydrogen into air; aniline dye into water, and gold into lead. As stated on p. 57, the molecules seem to lead a more or less independent existence, and the space between the molecules furnishes accommodation for the introduction of other particles. A study of the physical and the chemical properties of matter has thus led to one conclusion. **Matter is discrete, not continuous; and it is made up of minute particles called molecules.** This hypothesis is called the molecular theory of matter.

§ 5 The Kinetic Theory of Molecules.

Are the molecules stationary or in motion? Here again the phenomenon of diffusion has led us to further assume that the molecules are in rapid motion. How could gases diffuse one into the other in such a remarkable way if the molecules were at rest? Diffusion and the fact that a mixture of gases with different specific gravities shows no signs of

settling, compel us to assume that the molecules are in a state of incessant motion, and that they are travelling in all directions. In solids, the motion of the particles must be greatly hampered by adjacent molecules. The low compressibility of solids, and the comparatively slow rate at which one solid diffuses into another, shows that the molecules of a solid have a comparatively low mobility One molecule can only get away from contact with another molecule very very slowly, if at all The fact that most solids retain their shape for indefinitely long periods, unless prevented by chemical, mechanical, or physical actions, shows that the molecules of solids have a very limited mobility—*e.g.*, some ancient jewellery appears to be the same now as when first engraved.

The molecules of a liquid seem to have more freedom than solids. The molecules are sufficiently mobile to allow the liquid to quickly take up the shape of the vessel which contains it A molecule of a liquid can, in time, travel to any part of the liquid mass. Its course is necessarily slow, because it must be continually abutting against other molecules.

On the other hand, the molecules of a gas seem to lead a more or less independent existence They appear to be continually moving with a great velocity in sensibly straight lines in all directions. The molecules in their travels must be continually colliding with one another and bombarding the walls of the containing vessel. Thus the molecules continually change their speed and directions.

It is clear that an outward pressure must be exerted on the sides of the vessel every time a molecule strikes the boundary walls The moving molecules must be perfectly elastic so that after each collision they rebound with the same velocity as before, otherwise, their momentum would decrease with each collision, and the pressure of a gas would decrease with time, which it does not. Hence, it is inferred that the molecules are in a state of perpetual motion The preceding assumptions suffice for some important deductions which enable the condition of the molecules of a gas to be inferred with some degree of probability

§ 6 The Kinetic Theory and Boyle's Law

What *is* must be studied before what *was* can be inferred Precedent states remain visionary unless they can be linked to actual and observable conditions —A. M CLERKE.

Assume that a closed vessel contains n molecules, and that the ceaseless cannonade of innumerable molecules on the walls of the vessel produces an average pressure, p Imagine n similar molecules to be squeezed into the same vessel This will double the number of impacts on the sides of the containing vessel so that the pressure will rise from p to $2p$ The concentration of the gas will also be doubled This is nothing but another way of stating Boyle's law

The same result can be obtained another way Suppose a mass m of gas containing n molecules be confined in a cube with edges each l cm long, and that the molecules are moving with an average velocity V Although the molecules travel about in every conceivable direction it is fair, for purposes of calculation to consider the molecules are divided into three equal sets with velocities parallel to three adjacent sides of the cube At any instant, therefore we assume that $\frac{1}{3}n$ molecules are travelling with a velocity V parallel to any particular edge, and therefore perpendicular to the two corresponding faces of the cube One molecule moving with a velocity V will take l/V seconds to pass from side to side, and it

will therefore strike a side $\frac{1}{2}V/l$ times per second At each collision with the face of the cube the velocity of the molecule is reversed in direction so that its momentum changes from mV to $-mV$, that is, its momentum changes $2mV$ The total change of momentum by $\frac{1}{3}n$ molecules striking a side $\frac{1}{2}V/l$ times per second will therefore be the product $\frac{1}{2}V/l \times 2mV \times \frac{1}{3}n$, or $\frac{1}{3}nmV^2/l$ This measures the total force or pressure exerted on one face of the cube But the total surface of one face of the cube is l^2 Hence, the total pressure per unit area is $p = \frac{1}{3}nmV^2/l \div l^2 = \frac{1}{3}nmV^2/l^3$ But l^3 represents the volume v of the cube Hence

$$pv = \frac{1}{3}nmV^2$$

If the number n, the mass m, and the average velocity V do not change, the expression $\frac{1}{3}nmV^2$ is constant, and hence the product pv is constant This is Boyle's law

The effect of molecular attraction —If the molecules have appreciable cohesion, or attraction for one another, they will move in curved, not in straight paths Doubling the number of particles per unit volume will not then give exactly twice the number of impacts on the boundary walls. When the molecular attraction is marked, the product pv must be *less* than corresponds with Boyle's law Molecular attraction deflects some of the molecules from the straight path so that they do not strike the walls of the vessel under conditions where they otherwise would This appears to be the case with carbon dioxide, and most gases which have a smaller apparent volume v, or a smaller value of pv, that is, a greater concentration than corresponds with an increase of pressure as described by Boyle's law This is illustrated by the downward slope of the pv curves, Fig 26, for carbon dioxide below 150 atmospheres pressure

The effect of the size of the molecules —The small reduction in volume which occurs when a gas is highly concentrated is explained in the following way Under great pressures the volume of the molecule becomes comparable in magnitude with the space through which the molecule can move The volume of the space in which the molecules move is alone reduced by pressure, and therefore only part of the total volume occupied by the gas can be reduced by pressure Hence, at high pressures the apparent volume, and the product pv appear to be greater than is described by Boyle's law With hydrogen, for instance, when the pressure is doubled, the volume is not quite halved The same remark applies to other gases, *e g*, carbon dioxide, at great pressures. This is illustrated by the upward course of the curves, Fig 26

The kinetic theory and Graham's law —This relation (p 105) follows from the above discussion—$pv = \frac{1}{3}nmV^2$ The density of a gas is the mass of unit volume or $mn = D$ Hence from the preceding relation, $p = \frac{1}{3}DV^2$ When the pressure is constant, the velocity V will be inversely proportional to the square root of the density D, for $V^2 =$ constant $\div D$, etc. This is Graham's law

§ 7 The Kinetic Theory and Charles' Law and Avogadro's Hypothesis.

The kinetic theory and Charles' law.—Heat is generally considered to be a mode of motion of the molecules of matter The speed of the molecular motion determines the temperature If the speed increases, the number of molecular impacts on the boundary walls also increases if the volume remains constant, or the volume increases if the pressure remains constant It is now necessary to introduce an important assumption Two gases are in thermal equilibrium when the total

kinetic energies of the molecules are the same. Since real gases—which exert no chemical or physical action on one another and which are under the same conditions of temperature and pressure—can be mixed without change of temperature or pressure, it is assumed that the molecules of equal volumes of two gases at the same temperature and pressure possess the same total kinetic energies We have seen[1] that the total kinetic energy of a gas is proportional to the product *pv* Hence, if the temperature be altered, pressure remaining constant, the kinetic energy (*i e.* temperature) must alter to the same extent, and hence also the volume. Otherwise expressed, if the pressure remains constant, the same alteration of temperature will alter the volume to the same extent. This is Charles' law

The kinetic theory and Avogadro's hypothesis —From what has just been stated, it follows that equal volumes of two gases at the same temperature and pressure have the same value for the product *pv* Hence also the total kinetic energy of the one gas will be equal to the total kinetic energy of the other, or the product $n_1 m_1 V_1^2$ for one gas will be equal to the product $n_2 m_2 V_2^2$ for the other But the average kinetic energy per molecule in the two systems will be equal if the temperature is the same, and hence, $\frac{1}{2}m_1 V_1^2 = \frac{1}{2}m_2 V_2^2$, or, by substitution in the preceding relation, $n_1 = n_2$ This is the symbolic way of saying that equal volumes of two gases under the same physical conditions contain the same number of molecules, that is, Avogadro's hypothesis (see p 56) It is possible to argue backwards from Avogadro's hypothesis, and deduce the assumption italicized above. The one is dependent on the other Remember therefore that, contrary to what some enthusiastic writers assert, Avogadro's hypothesis has rendered it necessary to introduce *an unknown and unverifiable assumption*[2] into our reasoning The kinetic theory should not be quoted as a *proof* that Avogadro's hypothesis is true

§ 8 Summary of the Kinetic Theory

> The phenomena are our data, and behind them we cannot go except in imagination —A SCHOPENHAUER

We can now summarize the assumptions of the kinetic theory—the term "kinetic," by the way, is derived from the Greek κινέω (kineo), I move

(1) *Matter is composed of a finite number of molecules In gases, the actual volume of the molecules is very small compared with the space not occupied by the molecules At great pressures, however, the relative size of the molecules must be taken into consideration*

(2) *The molecules of a gas are in a state of rapid perpetual motion in straight lines The molecules are continually colliding against the walls of the boundary vessel and against one another*

[1] Magnitudes proportional to the same thing are proportional to one another

[2] According to J C Maxwell (1879) " If the system is a gas, or a mixture of gases not acted on by external forces, the theorem that the average kinetic energy for a single molecule is the same for molecules of different gases is not sufficient to establish the condition of equilibrium of temperature between gases of different kinds, such as oxygen or nitrogen, because when the gases are mixed we have no means of ascertaining the temperature of the oxygen and nitrogen separately We can only ascertain the temperature of the mixture by putting a thermometer in it "

(3) *The molecules are perfectly elastic and rebound after a collision without any loss of momentum.*

(4) *The molecules of gases do not always move quite independently of one another since some molecules have a slight attractive force one for the other. This becomes appreciable with increasing concentrations*

(5) *Two gases are in thermal equilibrium when the average kinetic energies of the molecules of the two gases are the same*

The kinetic theory and the corresponding molecular theory of liquids and gases have been of great service in helping chemists to form mental pictures of many processes which would be otherwise too difficult to conceive clearly No one pretends that the picture corresponds with reality, but it has been of great assistance in applying the method of deduction and verification (p 5) The theory has its faults, at present, it throws no light on many of the properties of gases, while the applications to liquids and solids have scarcely been touched A great deal of work remains to be done There is a school of chemists which repudiates the kinetic theory, as an exhausted, moribund hypothesis. As a matter of fact, the kinetic molecular theory still promises to live long when we get strong enough to grapple with its many difficulties.

A. D Risteen (1895) has compared the results of observation with the deductions from the kinetic theory in double columns. The following is modified from his scheme

Results of Theory	Results of Observation
1 The molecules of a gas are all alike	1 Gases are homogeneous and show no signs of settling, nor can the molecules of any particular gas in general, be separated by diffusion, into gases with different properties A special case—dissociation—will be discussed later
2 Molecules are at relatively great distances apart, and in constant motion in straight lines	2 The compressibility, permeability, and diffusivity of gases is great The incompressibility of gases at high pressures is supposed to be due to the abnormal crowding of the molecules
3 In a given mass of molecules, the product pv is proportional to the *average kinetic energy per molecule*	3 In a given mass of gas the product pv is proportional to the absolute *temperature, etc This includes the* laws of Boyle, Dalton, and Charles
4 Diffusion	4 Graham's law
5 The average *kinetic energy* is constant *for every set of molecules in a mixture* of gases	5 So far as we can tell, the *temperature* of each constituent of a mixture of gases is the same (see preceding footnote)
6 If two sets of molecules have the same kinetic energy, and the same pressure, they contain the same number of molecules per unit volume	6 Avogadro's hypothesis, and hence also Gay-Lussac's law (This is not a result of observation, but it has been inferred independently from purely chemical reasons)

The first inkling of the idea that the observed properties of matter may be due to motion of its constituent particles has been traced back to Democritus and Lucretius (p 35) The idea did not develop into a

physical hypothesis until R Hooke (1676), and D Bernoulli (1738), suggested that gaseous pressure must be due to the impact of the molecules on the sides of the containing vessel The work of T Herapath (1821), J P Joule (1850), R Clausius (1857), J C Maxwell (1860), and others played important parts in the subsequent development of the theory

§ 9 Ultramicroscopic Particles

> We are face to face with this extraordinary situation the molecule has ceased to be a theoretical abstraction—it has become a visible and tangible reality, for we can not only see it, but also "manipulate" it—not, indeed, with our hands, but by means of heat, and electricity, and the air pump—E E FOURNIER D'ALBE

In dealing with particles in an extremely fine state of subdivision, the millimetre is an inconveniently large standard of reference The symbol μ—pronounced "mu"—is employed for the thousandth of a millimetre, so that 0 001 mm $= 10^{-3}$ mm $= 1\mu$, and $\mu\mu$—pronounced "double mu" or "millimu"—is used for a millionth of a millimetre, such that 0 000001 mm $= 10^{-6}$ mm $= 1\mu\mu$, and $0\ 001\mu = 1\mu\mu$.

Ultramicroscopy —In practice a good microscope will not clearly resolve particles much smaller than $\frac{1}{4}\mu$ in diameter, and the term **ultramicroscopic particles** is applied to particles smaller than this limit The ultramicroscopic particles cannot be seen with a powerful microscope illuminated in the ordinary manner, because the light bends round the minute particle and enters the eye just as if the particle did not exist. If the particles be illuminated by a lateral beam of light, their very smallness enables them to scatter the light, so that their presence can be inferred from the fact that each particle is surrounded by visible diffraction rings, just as surely as the presence of smoke indicates fire The motes dancing in a beam of sunlight would be invisible but for this phenomenon

Clear solutions, with particles too small to be resolved by the most powerful microscope, appear more or less opalescent when a beam of converging light is focused into the solution A solution free from these particles would not produce the opalescence, and such a solution is said to be "optically empty" This is the so called **Tyndall's optical test** The sensitiveness of J Tyndall's optical test has been greatly developed by the use of a microscope—called the ultramicroscope—by H. Siedentopf and R Zsigmondy In the so called **ultramicroscope** an intense beam of light—arc light, or, better, a beam of bright sunlight—is focused into the liquid under examination, so that the light enters the liquid at right angles to the direction in which it is viewed under the microscope In one of the earliest experimental methods (1900) of ultramicroscopy, a beam of sunlight was reflected from a mirror, *M*, Fig 38, through a lens, *L*, and focused in the trough of liquid under examination in the field of a microscope If transmitted light be used, the eye is dazzled by the profusion of light, and it cannot distinguish the slight differences of brilliancy caused by the diffraction of light by the small particles, just as it is impossible to see the stars by daylight The later forms of the instrument are more complicated than this, though the principle is the same

While the opalescence produced by Tyndall's optical test merely shows

that a solution contains a number of distinct individual particles in suspension, the ultramicroscope enables the *individual* particles to be detected under conditions where the most powerful microscope would fail to reveal any sign of non-homogeneity. When viewed in the ultramicroscope, the ultramicroscopic particles appear as glittering discs of light with a dim or dark background. A solution may thus appear perfectly homogeneous when viewed under the most powerful microscope, and yet appear distinctly heterogeneous when viewed under the ultramicroscope.

The particles which can be perceived in the ultramicroscope are more or less approximately the same order of magnitude as the molecules themselves For instance, ultramicroscopic particles of colloidal gold, 1 7 $\mu\mu$, have been measured, and, according to Lobry de Bruyn, the estimated size of a molecule of soluble starch in solution is 5 $\mu\mu$; a molecule of chloroform is roughly 0 8 $\mu\mu$, according to G Jäger, and a hydrogen molecule

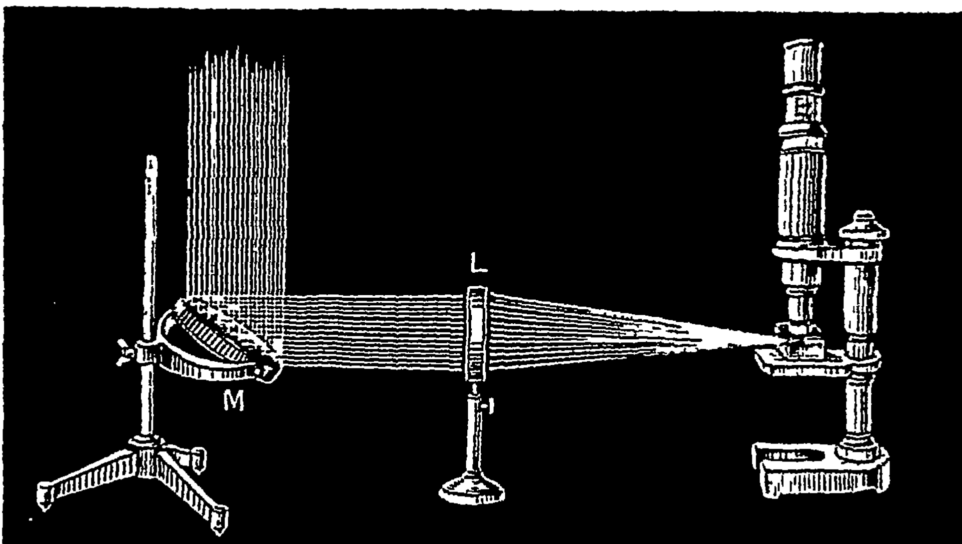


FIG 38 —Early Form of Apparatus for Ultramicroscopy.

is roughly 0 1 $\mu\mu$, according to O E Meyer Hence particles smaller than the complex molecule of soluble starch have been perceived.

The definition of solutions —Solutions are usually defined as "homogeneous mixtures which cannot be separated into their constituent parts by mechanical means (filtration through paper or decantation after settling)" This definition forces us back to the distinction between homogeneous and heterogeneous mixtures, and this, in turn, upon the sensitiveness of the tests for homogeneity A solution may appear clear and homogeneous, the particles in solution may not be separable by the ordinary methods of filtration, and the substance in the solution may remain suspended an indefinite time, and yet when Tyndall's optical test is applied, an opalescence will prove that minute particles are in suspension, and the ultramicroscope will enable the particles to be recognized as distinct individuals There are all possible gradations between liquids carrying rapidly settling particles in suspension, and liquids which carry

particles in suspension an indefinite time without settling, and in which the particles are so small that they can only just be perceived by the ultramicroscope Consequently, if the above definition of a solution be accepted, every time the sensitiveness of the method for detecting non-homogeneity is increased, a certain number of solutions previously classed as homogeneous will probably appear heterogeneous This difficulty can be partially overcome by arbitrarily restricting the term "solution," and defining Solutions are mixtures which appear clear and homogeneous in ordinary daylight, and which cannot be separated into their constituent parts by ordinary mechanical processes of filtration through paper and decantation after settling This subject will be taken up again in later chapters.

The Brownian movements —If water in which a little lycopodium—that is, the spores of the club moss—is suspended be examined under the microscope, the small particles appear to be incessantly vibrating with a slow trembling motion The phenomenon is named—*the Brownian movement*—after its discovery by R Brown in 1827 Experiment has shown that the motion cannot be due to convection currents set up by small differences of temperature or pressure, or to any known influence outside the liquid. The cause of the motion must be sought in the liquid itself.

The phenomenon is demonstrated as follows Rub a fragment of gamboge for a moment on an ordinary 3×1 glass slip and place a couple of drops of water on the slip where the gamboge has been rubbed Gently push a cover glass up to the edge of the gamboge The brisk motion of the particles can now be readily seen through a $\frac{1}{6}''$ objective and a dark ground illumination

The kinetic theory of molecular motion seems to furnish the only admissible explanation of the phenomenon It is supposed that owing to the perpetual movements of the molecules of the fluid, the moving molecules are continually striking the particles, thus driving them irregularly, to and fro, up and down, in the liquid. As might be expected, the incessant movements become more and more vigorous the smaller the particles There is a big contrast between the apparently sluggish movements of lycopodium, and the vivacious motions of the ultramicroscopic particles of, say, Faraday s gold. The latter are described by R Zsigmondy somewhat as follows "The particles move with astonishing rapidity A swarm of gnats in a sunbeam will give an idea of the motion The particles hop, dance, jump, dash together and fly away from one another so that it is difficult to get one's bearings" To this must be added the fact that if the composition of the liquid remains unchanged, the motion in the liquid continues an indefinite time without ceasing

By studying the movements of the fine particles of gamboge—that is, the dried latex of the *Garcinia morella*—suspended in water, and of extremely fine particles of silver dust obtained by striking an electric arc between silver poles—suspended in air, it has been proved that the distribution of the particles, their velocities, and the frequency of their collision is the same as the kinetic theory assumes to be the case with the particles of a gas The Brownian movement is thus an expression of the molecular movements usually attributed to the molecules of matter In fine, the experimental facts go very near towards establishing the validity and essential reality of the molecular kinetic theory as an explanation of the properties of matter

§ 10. Magnitudes in the Molecular World.

The above descriptions give no idea of the order of the magnitudes we are dealing with The kinetic theory allows these magnitudes to be approximately computed For air, at atmospheric pressure, and 0°, the calculations furnish roughly —

1	Diameter of a molecule	6×10^{-7} cm, 24×10^{-9} inch, 0 6 $\mu\mu$
2	Number of molecules	6×10^{18} per c c.; 24×10^{19} per cu in
3	Distance traversed between two collisions	0 00001 cm, 0 000004 in, 10 $\mu\mu$
4	Collisions per second	5000,000,000
5	Velocity per second	45,000 cm, 1500 feet

Most of these numbers convey no meaning to the mind because they are utterly beyond the range of our comprehension The following considerations will serve to emphasize our inability to form a clear concept of the "scale of magnitudes" in the "world of molecules" *First* A normal human eye, at a distance of 10 inches, can see objects $\frac{1}{250}$ inch in diameter, with a good microscope objects not much smaller than $\frac{1}{80000}$ inch in diameter can be clearly seen, but this is nearly 5000 times the magnitude of the molecule of an element It would take about 40 000 000 molecules, touching one another, to make a row an inch long *Second*, If all the molecules in a cubic inch of a gas were laid in a row, touching one another, they would form a line about 35,000,000 miles long, and this line would extend more than 1000 times round the earth *Third*, If the gas were magnified on such a scale that a molecule was an inch in diameter, each cubic foot would contain about one molecule, and a molecule would then travel about *100* feet before it collided with another *Fourth*, It would take about 53 years, counting at the rate of three per second, 24 hours a day, to count the number of collisions—5000,000,000—made by a molecule with its fellows every second *Fifth*, A molecule travels at the rate of nearly a quarter of a mile per second

§ 11 Brown's Kinetic Theory of the Atoms.

Like the planets and satellites of the solar system, the atoms of a molecule are in harmonious stable movement —D MENDELEEFF

1 Do the atoms of the molecules of a compound retain their individuality? It may be quite true that the properties of a compound are mainly determined by the character of the constituent elements, yet, it is not to be supposed that there is necessarily any resemblance between the properties of the elements and of their compounds For instance, the properties of a molecule of, say, water are very different from the properties of the constituents hydrogen and oxygen Although the atoms of a compound molecule do not enjoy a separate external existence, yet, *within* the molecule, the atoms are probably distinct, self contained, and self-existent, as Lucretius would have expressed it, they are "strong in their solid singleness" The individual properties of the atoms, however, are not always unrecognizable in the properties of the molecules of their compounds J Larmor (1908) has well said

It becomes increasingly difficult to resist the simple view that chemical combination involves an arrangement of the atoms alongside each other under steady cohesive affinity, *the properties of each atom being somewhat modified, though not essentially, by the attachment of the others*, and that the space formulæ of chemistry have more than an analogical significance The many instances in which the physical properties of the compound molecule can be calculated

additively[1] with tolerable approximation from those of the constituent atoms, are difficult to explain otherwise

2 Are the atoms of a molecule at sensible distances apart? It is sometimes asserted that the atoms are at "insensible" distances apart, and that the atoms of a molecule are accordingly very close together These statements have given rise to a misconception, for if the size of the atom be taken as a standard of reference it is probable that in the molecule the distances of the atoms from one another are comparatively great

3 Are the atoms of a molecule at rest or in motion? Some circumstantial evidence bearing on this question will be discussed towards the end of this book S Brown (1843) and D Mendeléeff (1868),[2] like many previous chemical philosophers, picture a complex molecule as a kind of miniature solar system with the atoms whirling about one another at great speeds. Like the planets and the satellites, the atoms are supposed to be "endowed with an everlasting motion." The atoms are further supposed to be held in position, and to move in definite orbits owing to their attraction for one another, just as the planets and satellites move in definite orbits owing to the action of gravitational forces. Mendeléeff, like Brown, is an enthusiast, he says

> Chemically, the atoms may be likened to the heavenly bodies, the stars, sun, planets, satellites, etc The building up of the molecules from atoms, and of substances from molecules is then conceived to resemble the building up of systems, such as the solar system, or that of twin stars, or constellations from individual bodies This is not a simple play of words in modern chemistry, nor a mere analogy, but a reality which directs the course of all chemical research, analysis, and synthesis

According to this view, a two atom molecule of hydrogen, H_2, iodine, I_2, or oxygen, O_2, might be depicted as a binary star—that is, as a pair of stars Each atom in the molecule rapidly revolves about the other in a regular orbit—an attempt has been made to illustrate the idea in Fig 116, a molecule of water, H_2O, would be represented by three atoms revolving in a similar manner, and a molecule of sulphuric acid might be depicted as a complex system with a central revolving sulphur atom around which the other atoms whirl in definite orbits. First would come two oxygen atoms representing the nucleus SO_2, outside these would encircle two oxygen atoms each with a revolving hydrogen atom as satellite The imaginary picture so obtained would be a kinetic model of the molecule $(HO)_2{=}S{=}O_2$, or H_2SO_4 The chemist determines the constitution of these tiny systems by a process which Martin has compared with the plucking of, say, the earth and moon from the solar system, or by replacing one planet by another and observing the disturbing effects of the transposition on the whole system The case of sulphuric acid will be discussed later A kind of orrery would therefore give a better idea of the structure of a molecule than the crude plane formulæ usually employed. By this analogy, the planets Mercury and Venus represent single

[1] ADDITIVE PROPERTIES —Additive properties depend on the nature of the atoms in a molecule Each atom exerts its own specific influence whatever be its state of combination. Numerous examples will occur later—molecular weight, specific heat, crystalline form, etc, see also pp 572 and 573

[2] T Bergman and G L L de Buffon both abandoned the theory as impracticable because they failed to realize the importance of the second question indicated above

atoms; the Earth, Jupiter, and Saturn with their moons represent radicles—each composed of several distinct atoms so as to form a small subsystem complete in itself. All these individuals and sub systems are linked to one another so as to form a balanced or stable molecular system, in some respects analogous with the solar system.

4. Valency.—Supposing Brown's and Mendeléeff's speculations were to be established by unassailable evidence, that would not alter the value of graphic or constitutional formulæ. So far as these formulæ are concerned, it really makes little difference whether the atoms are actually attached to one another, or whether they are held in position by their mutual attractions while they are revolving about a centre of stability. Indeed, some assume that the conditions—temperature, light, or electricity—necessary for the formation of a stable system determine whether a given atom can form a stable system with 1, 2, 3, ... other atoms; otherwise stated, the valency of an element is determined by the necessity for harmonizing the peculiar motions of the combining atoms to form a stable molecular system. S. Brown expressed the same idea in 1843; he said: "The conception can perhaps be made still more lucid by the counter statement in astronomy that a sun cannot be overloaded with planets." Brown's view of valency shows that it is not necessary to postulate a distinct force emanating from the atoms in order to explain how, say, HCl forms a stable molecular system, while HCl_2 and H_2Cl do not form stable molecular systems. If such systems were momentarily formed, the supernumerary atoms would be immediately flung off. There may, of course, be a number of different stable systems corresponding with the different stable molecules of, say, iron and chlorine, $FeCl_2$ and $FeCl_3$. The plausibility of this hypothesis, of course, is not a proof that it is true.

5. The energy of the atoms.—Each elementary atom, as we have seen, presumably has its own definite charge of energy. This energy probably exists in the form of atomic motions, so that when one atom "unites" with another atom, each atom possibly gives up a part of its energy, or "absorbs" energy from some external source, so that the motions of the one atom may be co-mingled with the motions of the other atoms to form a stable molecular system.

6. What makes the atoms and molecules move? We do not know! How can matter of itself initiate motion, and particularly motion in a harmoniously working system? *Ignoramus*. In the words of C. Kingsley, "Everywhere, skin deep below our boasted science, we are brought up short by mystery impalpable and by the adamantine walls of transcendental forces and incomprehensible laws." Consequently, the kinetic theories of atoms, of molecules, of the planetary systems, and indeed of the solar system itself, all prescribe or postulate an initial state of motion which is self-sustained and self-regulated. *Guesses at the birth-history of these motions have been whispered only by the poets.* Thus, in the oft-quoted lines of Virgil:

> Know first, the heaven, the earth, the main,
> The moon's pale orb, the starry train,
> Are nourished by a soul,
> A bright intelligence, whose flame
> Glows in each member of the frame,
> And stirs the mighty whole.

§ 12 The Effect of Molecular Attraction on an Expanding Gas —The Joule-Thomson Effect

If a gas, whose molecules exert no attraction on one another, be confined in a suitable vessel, and compressed, the mechanical work employed in compressing the gas is equivalent to the product of the pressure into the change in volume This energy is transformed into an equivalent amount of heat which raises the temperature of the gas. On the other hand, if the gas expands against atmospheric pressure, the gas will be cooled because the gas itself has done a certain amount of work equivalent to the product of the atmospheric pressure into the change in volume

No heat is developed when an ideal gas expands into a vacuum because no external work is done by the gas This was established experimentally by some early experiments by J L Gay-Lussac (1807), and by J P Joule (1845) Compressed air was allowed to expand into an evacuated vessel, and the result, as Joule expressed it, was as follows "No change of temperature occurs when air is allowed to expand in such a way as not to develop mechanical power" Hence, it was also inferred that no work is performed under these conditions against inter-molecular attractions.

Our study of Boyle's and Charles' laws has taught us that inter-molecular attractions occur with most gases. Hence, this latter deduction might be questioned The experiments, however were not sufficiently sensitive to detect the small change of temperature which occurs when a gas expands *in vacuo*, so that although no external work is done by the gas, internal work is done against molecular attraction The molecules are torn apart, so to speak, against the (feeble) attractive force drawing them together This involves an expenditure of energy—work must be done

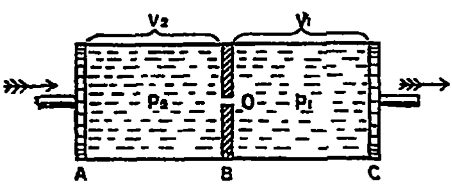


FIG 39 —Joule Thomson Effect.

Later, in a more delicate experiment, J P Joule and W Thomson (Lord Kelvin)—1852-62—forced a steady stream of gas under a pressure p_2 slowly along a tube, *A*, Fig 39, in the direction of the arrows, through a small orifice, *O*, where it expanded against the pressure p_1 For the sake of simplicity, suppose the tube *AB* has unit sectional area, and that it is made of some material which does not conduct heat away from the gas. Two phenomena occur (1) the gas is slightly heated by friction as it passes through the orifice *O*, and (2) the gas is cooled as it passes through *O* against a pressure p_1

Suppose a piston *A*, Fig 39, moves from left to right so as to drive a volume of air, v_2 at a pressure p_2 into the compartment *BC* The work done *on* the gas is obviously p_2v_2. Similarly, the work done *by* the gas as it pushes the piston from, say, *B* to *C* through a distance v_1 will be p_1v_1 Hence, if the gas obeys Boyle's law, we shall have $p_1v_1 = p_2v_2$, and there will be no variation of temperature of the gas on the side *AB* and *BC* If, however, work be done against molecular attraction during the expansion of the gas the work of expansion on the side *BC* will exceed the work of compression on the side *AB* The extra work will absorb heat from the

gas itself Hence, the gas on the side *BC* will be cooled below the temperature of the gas on the side *AB* In Joule and Thomson's experiments, the temperature of carbon dioxide, nitrogen, oxygen, and air fell about 1°, while the temperature of hydrogen gas rose about 0 039° above the temperature of the gas on the side *AB* If, however, the experiment be conducted at a lower temperature, hydrogen gas behaves like the other gases, and is cooled The change of temperature which occurs when a gas is driven through a small orifice is called the Joule-Thomson effect

§ 13 The Liquefaction of Gases.

When a gas, passing through an orifice *O*, Fig 39, and cooled by the Joule-Thomson effect, is made to circulate around the tube leading the compressed gas to the orifice, the gas issuing from the orifice will be cooled still more. The "self intensive" or cumulative systems for cooling gases, elaborated by C Linde, W Hampson, and C E Tripler, between 1894–95, are based upon this principle The idea will be understood after an examination of Fig 40 The air to be liquefied—freed from carbon dioxide moisture, organic matter, etc —enters the inner tube of concentric or annular pipes, *A*, under a pressure of about 200 atmospheres This tube is hundreds of yards long and coiled spirally to economize space By regulating the valve *C* the compressed air suddenly expands in the chamber *D* The air thus chilled passes back through the tube *B* which surrounds the tube *A* conveying the incoming air The latter is thus cooled still more The gas passes along to the pumps where it is returned with more air to the inner tube In this manner, the incoming air at 200 atmospheres pressure is cooled more and more as it issues from the jet *O* Finally, when the temperature is reduced low enough, drops of liquid air issue from the jet The tubes must all be packed in a non-conducting medium—wool, feathers, etc —to protect them from the external heat

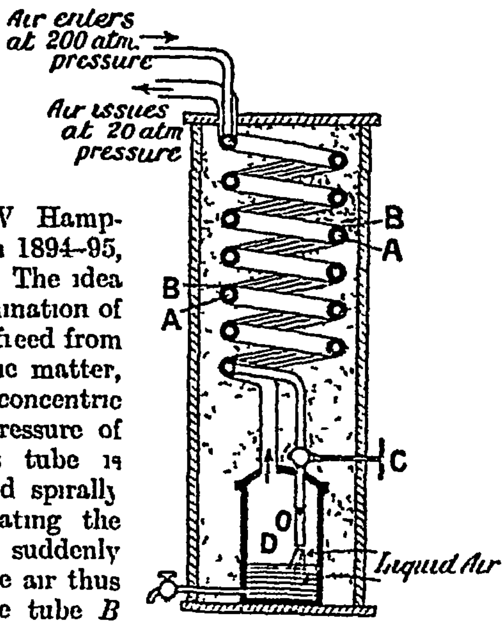


FIG 40 —Linde's Apparatus for Liquefying Air (Diagrammatic)

Preserving liquid air.—There is a far greater difference between the temperature of liquid air (about −190°) and ordinary atmospheric air, than between the temperature of ice and boiling water The preservation of liquid air is thus a far more difficult problem than would be involved in preventing cold water boiling away while surrounded by a steam jacket at 200° James Dewar solved the problem by keeping the liquid air in a

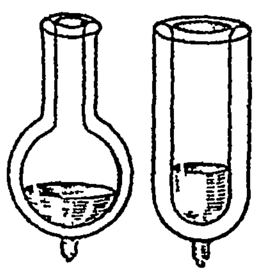


FIG 41 —Dewar's Flasks.

double (or triple) walled vessel with the space between the walls evacuated, Fig 41 Glass is a poor conductor, and a vacuum is a non-conductor Hence, the liquid in the inner vessel can receive heat only from above, and by radiation The glass walls of the evacuated space are also silvered to reduce the effects of radient heat. Still air is a very bad conductor, so that the open end of the vessel is plugged lightly with cotton wool in order to reduce the ingress of heat from outside to a minimum In this way, liquid air is transported by rail, etc, with a surprisingly little loss.

§ 14 The Manufacture of Oxygen and Nitrogen from Liquid Air

Linde's process—In Linde's process (1895), purified air is compressed to about 200 atmospheres, and driven along a pipe which divides at *A*, Fig 42, into two streams and then passes down the interior tubes of a double set of annular or concentric pipes similar to the worm tube, Fig 40 The two inner tubes finally unite into one single pipe, *B* The air then passes through a spiral *S*, *viâ* the regulating valve *R*, and finally streams at *C* into the collecting vessel. The action is here similar to that described in the process for the liquefaction of air, Fig 40 After a time, the air is liquefied in the collecting vessel, about the spiral *S* The more volatile nitrogen boils off more rapidly than the oxygen Hence, a gas rich in nitrogen passes up one of the two annular outer pipes as indicated on the left of Fig 42 The liquid rich in oxygen is kept at a constant level by means of the valve, and thus the rate at which the liquid air in the collecting vessel is allowed to boil is also regulated. The oxygen passes from this tube on the right of Fig 42 along the outer annular pipe, and finally emerges from the apparatus whence it is pumped into cylinders, etc, for use. If the valves are all properly regulated, the inrushing air is cooled by the counter currents of oxygen and nitrogen. The two latter gases pass along the tubes as indicated in the diagram. The tubes, etc, are all well insulated with non conducting materials—feathers, wool, etc By this process oxygen can be obtained as pure as is commercially desired, but the escaping nitrogen contains over 7 per cent of oxygen The original apparatus has been much improved, but Fig 42 illustrates the underlying principle very well. As G Claude has said "We must salute in this apparatus the archetype of all the later machines, for it was the first to demonstrate that the manufacture of oxygen from liquid air is commercially possible"

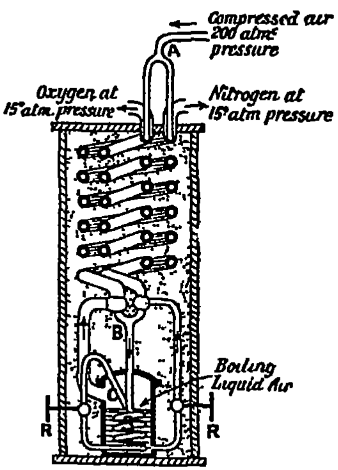


FIG 42—Linde's Apparatus for the manufacture of Oxygen from Liquid Air (Diagrammatic)

Claude's counter-current process of rectification—An improvement on Linde's process, by G Claude (1903), enables practically pure oxygen and nitrogen to be obtained When liquid air evaporates, the nitrogen—

more volatile than the oxygen—escapes first, and the gas which comes from the liquid during the earlier stages of the evaporation contains so little oxygen that it will extinguish a lighted taper, as evaporation continues, the escaping gas becomes richer and richer in oxygen until at last the escaping oxygen is almost free from nitrogen Similarly, if oxygen be bubbled through liquid air, the escaping gas contains about 93 per cent of nitrogen —oxygen condenses from the rising bubbles, and nitrogen takes its place

A diagrammatic sketch of Claude's apparatus is shown in Fig 42A The cooled and purified air enters the lower part of the apparatus at a pressure of about 5 atm and rises through a series of vertical pipes *P* surrounded by liquid oxygen, where it is partially liquefied The liquid containing about 47 per cent oxygen and 53 per cent of nitrogen drains into the lower vessel *A* The vapour which has survived condensation enters *B* and then descends through a ring of pipes *C* arranged concentrically about the set previously described Here all is liquefied The liquid which ultimately collects in this vessel *D* is very rich in nitrogen The pressure of the vapour in the central receptacle forces the liquid nitrogen to enter the summit of the rectifying column *E*, and the liquid, containing 47 per cent of oxygen, is likewise forced to enter the rectifying column at *F* lower down The pressures and rates of flow are regulated by the cocks *RR* The liquid nitrogen is 3° or 4° lower in temperature than the liquid rich in oxygen Nitrogen evaporates from the down streaming liquid, and oxygen condenses from the up streaming gases The heat supplied by the condensation of oxygen helps on the evaporation of nitrogen Consequently, the descending liquid gets progressively richer and richer in oxygen, and the ascending gases richer in nitrogen The liquid oxygen drains into the receptacle *G*, and is there evaporated by the latent heat of the gases condensing in the tubes Finally, oxygen containing from 2 to 4 per cent of nitrogen passes from the oxygen exit, and nitrogen containing 0 2 to 1 per cent of oxygen escapes at the top of the rectifying column

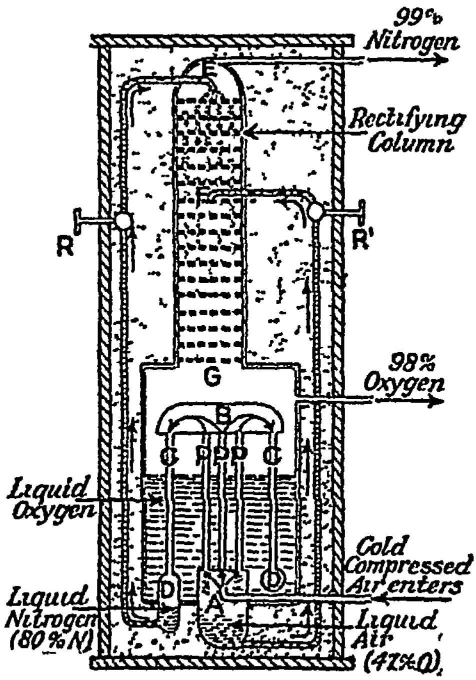


FIG 42A —Claude's Apparatus for the separation of Oxygen from Liquid Air (Diagrammatic)

These processes enable oxygen and nitrogen to be made comparatively cheaply—one ton of coal for driving the compression apparatus is said to furnish one ton of oxygen and four tons of nitrogen As Linde says, "the heat is eliminated from the air exclusively by the expenditure of internal work," that is, the work required for the liquefaction of these gases is solely spent in separating the molecules of the gases from one another against their inter-molecular attractions

Question.

On the basis of the Kinetic Theory deduce a relationship between the pressure of a gas and the velocity and density of its molecules Calculate the molecular weight of an unknown gas which under precisely similar conditions, takes 1 117 times as long as oxygen to diffuse through an aperture —*Sheffield Univ*

CHAPTER VIII

OXYGEN

Atomic weight, O = 16, molecular weight O_2 = 32, bi or quadri valent Melting point, $-227°$, boiling point, $-182 5°$, critical temperature $-119°$ Relative vapour density (H_2 = 1), 31 762, (air = 1) 1 1045 One litre of oxygen at 0°, 760 mm, and at latitude 45° at sea level, weighs 1 4292 grams, and 1 gram occupies 0 6997 litre

§ 1 Oxygen—Occurrence and History

Occurrence—About one fourth of the atmospheric air, by weight, consists of free oxygen, and water contains nearly 89 per cent of combined oxygen Oxygen also forms a material part of rocks It is estimated that nearly one half of the total weight of the rocks which make up the half-mile crust of the earth is oxygen, see p 9

History—Karl Wilhelm Scheele's laboratory notes, preserved in the Royal Academy of Science, at Stockholm, are said to prove that Scheele discovered oxygen gas some time before 1773 Scheele called the gas "fire air" and "vital air" Scheele made oxygen by heating red oxide of mercury, sulphuric acid and manganese dioxide, nitre, and some other substances. Scheele did not publish an account of his work until 1777 Meanwhile Joseph Priestley independently prepared the same gas, which he called "dephlogisticated air," while examining the effect of heat upon a great variety of substances confined in a cylinder (*A*, Fig 43) along with mercury, and inverted in a trough of mercury, somewhat as in Fig 43 Priestley focused the sun's rays upon the different substances by means of a "burning lens of 12 inches diameter, and 20 inches focal distance" Priestley announced his discovery of oxygen in these words "On the 1st of August, 1774, I endeavoured to extract air from *mercurius calcinatus per se*,[1] and I presently found that by means of this lens, air was expelled from it very readily Having got about three or four times as much as bulk of my materials, I admitted water to it and found that it was

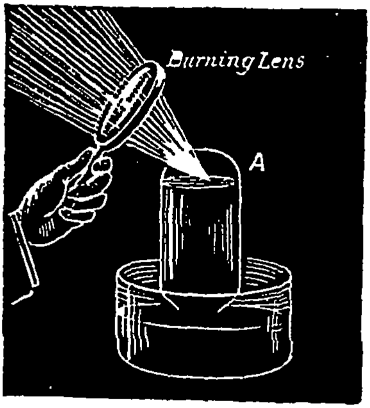


FIG 43—Priestley's Experiment

[1] That is, mercuric oxide, or red oxide of mercury

not imbibed by it But what surprised me more than I can well express, was that a candle burned in this air with a remarkable brilliant flame" Many erring steps have stumbled on the threshold of the discovery of oxygen, for instance, Eck de Sultzbach, in 1489, knew that red oxide of mercury gave off a "spirit" when heated, had he named and isolated the "spirit" he would have been credited with the discovery of oxygen There are also indications in old books that the Greeks knew about oxygen in the fourth century, and that the Chinese were acquainted with the gas long before Priestley's and Scheele's experiments

§ 2 The Preparation of Oxygen

Mercuric oxide process—When a supply of oxygen is required for experimental purposes, the apparatus can be arranged differently from Priestley's plan The mercuric oxide can be placed in a hard glass tube *A*, Fig 44, bent as shown in the diagram, and fitted with a cork *B*, and bent-glass delivery tube *C* One end of the delivery tube dips in water, Fig 9, or in special cases, in mercury, Fig 44 The mercury gas-trough shown at *D* can be worked with 5 lbs of mercury, and it is convenient for collecting small quantities of gas when it is desirable to keep the gas out of contact with water In most cases, of course, the ordinary water pneumatic trough, Fig 9, will be used. The temperature of the vessel containing the mercuric oxide is gradually raised. The air in the tube is first driven off and allowed to escape Later, globules of mercury begin to collect in the upper part of the tube, and oxygen is given off The mercuric oxide decomposes: $2HgO = 2Hg + O_2$. The oxygen is collected for examination, the mercury collects in the bend *E*, and there is no risk of mercury running back on to the hot glass and cracking the tube 10 grams of mercuric oxide give not quite half a litre of oxygen

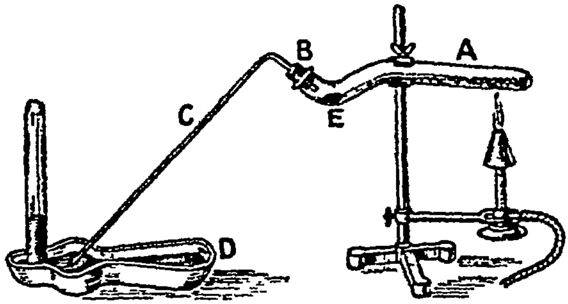


FIG 44—The Preparation of Oxygen

Many other oxides are available—*e.g* gold and silver oxides decompose at lower temperatures than mercury oxide, while manganese peroxide (pyrolusite) decomposes at a higher temperature Unlike silver, mercury, and gold oxides, manganese oxide does not break down into the corresponding metal and oxygen, but rather into a complex oxide similar in composition to the mineral hausmannite—Mn_3O_4 The reaction is symbolized: $3MnO_2 = Mn_3O_4 + O_2$ Gold, silver, and mercuric oxides are not often used on account of the expense

The action of heat on potassium chlorate—Potassium chlorate is a white crystalline solid which melts to a clear liquid when heated to about 340° At about 10° higher the melted chlorate appears to boil, because bubbles of oxygen gas are copiously evolved The potassium chlorate is decomposing When the bubbling ceases, the molten mass begins to

"thicken" or solidify The potassium chlorate has decomposed into potassium perchlorate, potassium chloride, and oxygen If the temperature be raised still further—over 600°—the mass again melts to a clear liquid and the potassium perchlorate decomposes, giving off more oxygen The final products of decomposition are potassium chloride and oxygen Hence, potassium chlorate can be used in place of mercuric oxide for the preparation of oxygen gas Ten grams of potassium chlorate will give nearly 2¾ litres of oxygen The amount of oxygen given off by heating a definite weight of mercuric oxide or potassium chlorate can be determined by placing about a gram of, say, potassium chlorate, dried at 150°, in a hard glass tube *C*, Fig 45 Care must be taken that no chlorate sticks to the side of the tube or it may escape the action of heat The increase in weight of the tube before and after the introduction of the chlorate represents the amount of chlorate used After the chlorate has been heated, very gently at first, and afterwards very strongly, cool, weigh the tube, and also measure the volume of oxygen in the burette The manipulation with the burette is the same as described for Fig 32, p 94. The loss in weight of the tube represents the amount of oxygen which has been expelled, and this number will agree closely with the weight of the gas calculated from the volume measured in the gas burette, if the measurements are accurate

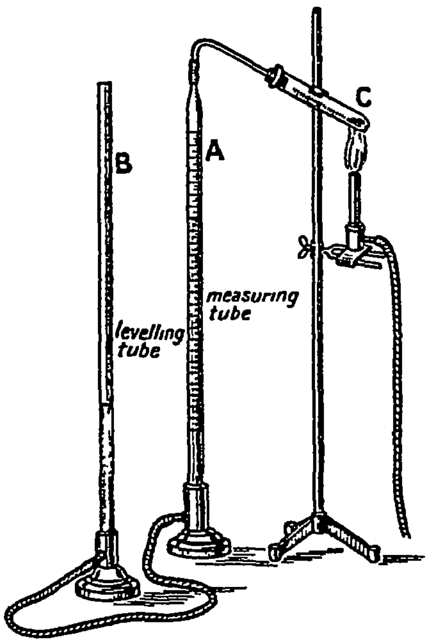


FIG 45 —The Determination of Oxygen evolved by heating Potassium Chlorate

The potassium chlorate decomposes completely at a much lower temperature if it be mixed with manganese dioxide Manganese dioxide, when heated alone, does not give off oxygen below 400°, potassium chlorate alone does not give off oxygen below about 340°, a mixture of the two gives off oxygen at about 200°. After the action, manganese dioxide still remains, but the potassium chlorate has decomposed into potassium chloride and oxygen. Manganese dioxide can be recovered from the residue by lixiviating the mass with water The water dissolves the potassium chloride, and leaves the manganese dioxide as a residue

If potassium chlorate be suddenly heated to a temperature above that at which decomposition occurs, the salt may detonate in an open vessel under ordinary pressure Some disastrous explosions have been produced by potassium chlorate M. Berthelot's experiment (1899) illustrates the explosive nature of this salt

One end of a glass rod is drawn out into a thread, and the narrow end is dipped several times in melted potassium chlorate so that each layer of salt solidifies before the rod is dipped again When a bead has been formed at the end of the rod, dip the rod into a test tube heated red hot at one end so that the salt is about a centimetre from the bottom of the tube Take care not to touch the sides of the tube As the chlorate melts, it slowly drops to the bottom of the test tube, each drop of chlorate as it falls explodes with a sharp detonation

Potassium chlorate process for making oxygen—For regular experimental work, oxygen is prepared by heating a mixture of potassium chlorate (not powdered) with its own bulk of manganese dioxide [1]—oxgyen mixture—in a wide-necked Florence flask or a retort, or a special copper "oxygen flask," [2] fitted with a wide delivery tube, because the gas is liable to come off rapidly in rushes The flask is best clamped while tilted slightly downward towards the mouth, as indicated in Fig 46, because a

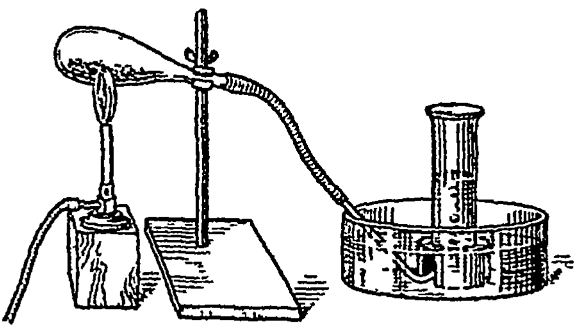


FIG 46—The Preparation of Oxygen

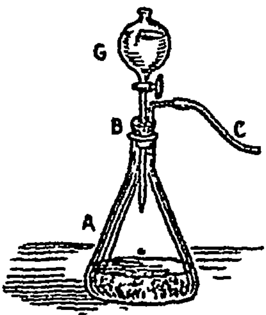


FIG 47—The Preparation of Oxygen

considerable amount of moisture is usually discharged from the mixture, and there is a risk of the moisture trickling back and cracking the glass The gas is collected over water as in the case of hydrogen

Peroxide method—A third method of preparing the gas depends upon the fact that sodium dioxide—also called commercially "oxone"—is decomposed by water into sodium hydroxide and oxygen $2Na_2O_2 + 2H_2O = 4NaOH + O_2$ Place about 10 grams of dry sodium dioxide in a dry 200 c c Erlenmeyer's flask, *A*, Fig 47. The flask is also fitted with a stopper *B* bored with two holes One hole is fitted with a delivery tube *C*, and the other hole with a tap funnel *G* containing water The water from the funnel is allowed to fall, drop by drop, on to the peroxide Each drop of water produces a definite amount of gas, so that the rate of evolution of the gas can be regulated by the rate at which water is allowed to drop from the funnel No external application of heat is required. 6¼ grams of the peroxide give about a litre of oxygen

Permanganate process—Many other methods are available for the preparation of oxygen Heating sulphuric acid with manganese dioxide, chromic acid, potassium dichromate, potassium permanganate, etc In the last case, heat a mixture of, say, 20 grams of potassium permanganate with 80–100 c c of dilute sulphuric acid (one volume of the concentrated

[1] If the manganese dioxide contains carbonaceous matters, an explosion may occur Hence the manganese dioxide should be tested by heating a little with potassium chlorate before a large quantity is heated

[2] 40 grams of the oxygen mixture may be used with a 250 c c flask.

acid with four volumes of water) in a flask with a delivery tube and safety funnel as in, say, Fig 94 Oxygen begins to come off when the temperature is about 50°, and continues in a steady stream Ten grams of the permanganate with between 40–50 c c of the dilute sulphuric acid give just over a litre of gas

Industrial preparation —The particular process to be employed must be determined by cost and convenience If but a few litres of gas, not specially purified, are required, cost is not very serious, and convenience is perhaps the most important factor, if pure oxygen be required, a complicated apparatus may be needed, and neither cost nor labour must be spared. An elaborate apparatus may be needed to remove traces of impurities—say, traces of ozone and chlorine from the oxygen Pure potassium chlorate alone will give a gas of a high degree of purity This method of preparation was used by Morley—p 46—in his work on the atomic weight of oxygen If large quantities of gas are needed, say for industrial purposes, the cost factor is of prime importance Generally speaking, the success of industrial operations depends upon the ability of the chemist to manufacture his products cheaply Oxygen was formerly made on a manufacturing scale by Brin's process (1881) This depends upon a very interesting reaction When barium oxide—BaO—is heated in air to about 500°, it is rapidly oxidized to barium dioxide $2BaO + O_2 = 2BaO_2$. If the barium dioxide be heated to a still higher temperature, 800°, the oxygen is given off and barium oxide remains as a residue $2BaO_2 = 2BaO + O_2$ The barium oxide can be reoxidized and used over and over again, provided the air be freed from carbon dioxide, organic matter, dust, and any substance which forms a compound with barium oxide which is not decomposed under the given conditions. The regulation of the temperature offered practical difficulties which were overcome by keeping the temperature constant in the vicinity of 700° Barium oxide is then transformed into the dioxide if the pressure of the atmosphere be about 2 kilos per square cm [1] The peroxide is decomposed into the oxide and oxygen at the same temperature under a reduced pressure—about 0 05 kilogram per square cm The gas pumped off under these conditions contained about 90–96 per cent of oxygen, and 4–10 per cent. of nitrogen Brin's process could not compete successfully against the cheaper method of preparation by the fractional distillation of liquid air (p 126) Nearly all the oxygen on the market is now obtained by the liquid air process Very little is obtained by the electrolytic process indicated on p 93 The oxygen is pumped into steel cylinders under a pressure of 100–150 atmospheres, and sold as "compressed oxygen" The gas may be obtained from the cylinders at any desired rate by opening the valve

§ 3 Catalysis

The action of manganese dioxide on the decomposing chlorate is very curious It acts as a stimulant. We do not know precisely how the manganese peroxide does its work, although we can form a rough idea of what is taking place. Many other oxides act similarly, but not quite so vigorously—*e.g* ferric, copper, cobalt, or nickel oxide may be used in place of manganese oxide It is quite a common thing to find that the

[1] Normally the atmospheric pressure is 1 033 kilograms per square cm

speed of reactions is accelerated or retarded by the presence of a "foreign" substance whose composition at the end of the reaction is the same as it was at the beginning We met two cases in connection with the combustion of hydrogen—platinized asbestos, and moisture These agents are conveniently grouped together as "catalytic agents," and the general phenomenon is called "catalysis" It must be clearly understood that "catalytic reactions" is simply a term for grouping those reactions whose speed is modified, or for those reactions which can be started by the presence of a small amount of a substance which is found to possess, at the end of the reaction, the same chemical composition as it had at the beginning The catalytic agent may be affected by interaction with the products of the reaction, etc —see "Consecutive reactions" (§ 5) The word "catalysis" itself explains nothing To think otherwise would lay us open to Mephistopheles' gibe

> A pompous word will stand you instead
> For that which will not go into the head

This means that too much trust must not be placed in words It is just when ideas fail that a word comes in most opportunely There is no difficulty in covering an obscure idea by a word so that the word appears to explain the idea In passing back from the word to the idea, it becomes easy to believe that the "subjective abstraction has an objective existence," or that because there is a word, something real must lie behind the word

These remarks about the term "catalysis" might be applied, *mutatis mutandis*, to many of the terms in common use in chemistry—"passive resistance," "chemical affinity," the "ions" of the ionic theory, etc. Ostwald ingeniously compares the action of a catalytic agent with the action of oil on a machine, or of a whip on a sluggish horse Ostwald, and his followers, believe that the reaction *must* be actually in progress before the catalytic agent can act This limitation is quite arbitrary and, so far as we can see, does not agree with all the facts Catalytic agents can start, accelerate, or retard the speed of chemical reactions.

§ 4 The Properties of Oxygen.

Oxygen, like air, is at ordinary temperatures, a colourless, tasteless, and odourless gas It is a little heavier than air

Litre of normal air (760 mm and 0°)	1 292 grams
Litre of oxygen (760 mm and 0°)	1 429 grams

Oxygen is appreciably soluble in water—100 volumes of water, at 0°, can dissolve nearly 5 volumes of oxygen under a normal pressure of 760 mm, and at 20° about 3 volumes of the gas are dissolved. Fish are dependent upon the air dissolved in water for the oxygen they need for respiration Animals are dependent upon the oxygen in air for respiration. A mouse soon dies if placed in an atmosphere deprived of oxygen Pure oxygen can be breathed for a short time without harm, and oxygen is used medicinally in artificial respiration in cases of suffocation, carbon monoxide poisoning, etc, where, owing to the enfeebled action of the lungs, the blood is not sufficiently aërated The prolonged inhalation of oxygen soon raises the temperature of the body dangerously high. An animal placed in ordinary or in compressed oxygen soon dies.

Metallic silver, gold, platinum, and palladium absorb oxygen at about 500°. Molten silver dissolves about ten times its volume of oxygen, and gives it up again on cooling. In cooling, a solid crust forms on the exterior surface; as the interior cools, the gas bursts through the solid crust driving out a spurt of the still fluid metal—the phenomenon is called the "spitting" of silver. Molten platinum behaves in a somewhat similar way.

Oxygen has been condensed to a bluish coloured mobile liquid at $-119°$ under a pressure of 50 atmospheres. If the temperature exceeds $-119°$, oxygen cannot be liquefied by any pressure however great. The smallest pressure which will liquefy oxygen at $-119°$ is 50 atmospheres. The temperature $-119°$ is therefore the critical temperature, and 50 atmospheres is the critical pressure of the gas. Liquid oxygen boils at $-182.5°$, pressure 760 mm. The liquid has a specific gravity of 1.13, that is, liquid oxygen is 1.13 times as heavy as an equal bulk of water. Liquid oxygen can be frozen to a pale bluish white solid not unlike snow in appearance. The solid melts at $-227°$, and has a specific gravity 1.43. With the notation used before

$$\text{Oxygen}_{\text{solid}} \overset{-227°}{\rightleftharpoons} \text{Oxygen}_{\text{liquid}} \overset{-182.5°}{\rightleftharpoons} \text{Oxygen}_{\text{gas}}$$

Liquid oxygen is strongly attracted by a magnet. Liquid oxygen furnishes an interesting explosive when mixed with charcoal; 3 cm. cartridges charged with one part carbon, one part petroleum, and eight parts of liquid oxygen were tried experimentally when cutting the Simplon tunnel. The chief objection is that the cartridges must be used within three minutes after charging, or the oxygen will evaporate. This objection might be an advantage under some circumstances.

Oxygen is used in conjunction with hydrogen for the oxy-hydrogen flame (*q.v.*), and with acetylene for the oxy-acetylene flame used in welding, etc. Oxygen is used in bleaching, in the oxidation and thickening of oils to be used in making varnishes, linoleum, etc.

The great chemical activity of oxygen is well typified by Priestley's quaint observation, indicated on p. 128. A glowing splint of wood ("cedar splints") when plunged into oxygen bursts into flame, the carbon of the wood being oxidized to carbon dioxide (CO_2). The inflammation of a glowing splint is often used as a test for oxygen. Oxygen alone has no action on clear lime water, but after a splint has burnt in the gas, the clear limewater becomes turbid. Oxygen combines directly with most other elements, particularly at elevated temperatures, forming oxides. Iodine, bromine, fluorine, gold, platinum, and argon and its companions do not combine directly with oxygen; but oxygen combines indirectly with all the elements excepting the argon group of elements, fluorine, and possibly bromine. If the metals be arranged in the order of their avidity or readiness to combine with oxygen, cæsium, potassium, and sodium will be found at one end of the series, while platinum and the argon family will be found at the other end.

The direct combination of oxygen with some of the elements can be illustrated by placing small dry pieces of carbon, sulphur, phosphorus in deflagrating spoons, heating them until combustion begins, and then plunging each into a jar of oxygen.[1] The glowing piece of charcoal burns

[1] Quick sealing fruit jars fitted with a deflagrating spoon make excellent gas jars for these experiments.

very brightly and forms a gaseous oxide—carbon dioxide, CO_2 Sulphur burns with a lavender-blue flame, forming gaseous sulphur dioxide—SO_2—which has the peculiar odour characteristic of burning sulphur The reaction is symbolized $S + O_2 = SO_2$, sulphur dioxide is soluble in water forming sulphurous acid—H_2SO_3—which reddens blue litmus solution—$H_2O + SO_2 = H_2SO_3$ The experiment can be conducted as recommended by F Rudorff, Fig. 48 The two-necked globe is corked at one end and filled with oxygen at the pneumatic trough in the ordinary manner, one neck is allowed to dip in a beaker of water as shown in the diagram When the deflagrating spoon, fitted with a tightly fitting cork, is inserted with the burning sulphur into the globe, the water, coloured with blue litmus, rises in the vessel as the sulphur dioxide is absorbed At the same time the litmus changes in colour, showing the formation of an acid during the burning of the sulphur Phosphorus burns in oxygen vigorously and brilliantly, forming a white cloud of phosphorus pentoxide—P_2O_5 The reaction is represented $4P + 5O_2 = 2P_2O_5$ The phosphorus pentoxide dissolves in water, forming phosphoric acid—H_3PO_4 The reaction is written $P_2O_5 + 3H_2O = 2H_3PO_4$ These reactions will be studied in more detail when the elements in question receive individual treatment

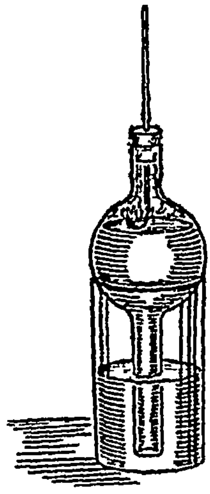


Fig 48—Rüdorff's Gas Jar

It might be added that dry sulphur, dry phosphorus, and dry carbon burn with great difficulty or not at all in dry oxygen In fact, perfectly dried substances often appear to be chemically inert, whereas they react vigorously if a trace of moisture be present

To show the combustion of iron in oxygen gas, tie a tuft of "steel wool" to the end of a stout iron wire by means of a piece of steel wire Heat the end of the wool in a Bunsen's flame, until incipient combustion begins, and quickly plunge it into a jar of oxygen on the bottom of which a layer of water, sand, or asbestos paper has been placed The wool burns with dazzling scintillations, the product of the reaction—iron oxide—falls to the bottom of the jar in fused globules When cold, the oxide of iron resembles a *blacksmith's hammer scale* It is called black or magnetic oxide of iron—Fe_3O_4 The reaction is usually written $3Fe + 2O_2 = Fe_3O_4$ The subject of oxidation and combustion will be resumed in a later chapter

§ 5 Consecutive Reactions.

Let us return to the action of heat on potassium chlorate The representation of a chemical reaction by means of an equation emphasizes the character of the initial and of the end products of the reaction, but it conveys no idea of the mechanism of the reaction—*how* the different materials interact to give the final products. There can be no doubt that quite a number of intermediate stages temporarily subsist before the drama of the reaction closes with the final act—the formation of the end products There is plenty of evidence leading us to infer the existence of a kaleidoscopic sequence of changing scenes during the progress of what are usually

considered simple reactions. Some suppose that water has no more right to representation in the chemical equation than the glass of the vessel in which the reaction occurs. As we progress in our studies, we shall find that water profoundly modifies the properties of most substances with which it is in contact—*e.g* the influence of moisture on the oxidation of hydrogen, sulphur, etc. The regular type of chemical equation shows but the beginning and the end of the reaction

As a result of quite a number of experimental investigations on the decomposition of potassium chlorate, and a study of the available circumstantial evidence, we are able to get, in imagination, a peep behind the curtain which hides the course of the reaction Firstly, it is not quite correct to say that the manganese dioxide is not changed in any way during the reaction because a microscopic examination of the manganese dioxide, before and after the reaction, shows that it has undergone a physical, if not a chemical, change—crystalline manganese dioxide apparently becomes amorphous. The manganese dioxide does appear to take part in the reaction in spite of the fact that it has the same chemical composition at the end as it had at the beginning Secondly, the manganese dioxide is probably oxidized by the decomposing chlorate to form one of the unstable higher oxides of manganese, exactly what oxide we do not know This uncertainty is expressed by writing the unknown oxide MnO_{n+2} where the numerical value of n is not known with certainty. This stage of the reaction can then be represented by the equation

$$\frac{n}{3}KClO_3 + MnO_2 = \frac{n}{3}KCl + MnO_{n+2} \qquad (1)$$

Thirdly, the unstable oxide produced by the oxidizing action of the potassium chlorate probably breaks down almost as soon as it is formed, regenerating the manganese dioxide, and liberating free oxygen

$$2MnO_{n+2} = 2MnO_2 + nO_2 \qquad (2)$$

The manganese dioxide so formed is again oxidized, and the oxide again decomposed regenerating manganese dioxide anew This cycle of changes continues until the potassium chlorate is all decomposed The opening and closing scenes are represented

$$2KClO_3 [+ MnO_2] = 2KCl [+ MnO_2] + 3O_2$$

Equations (1) and (2), expressed in the most general form, indicate that we are dealing with a reaction in which

$$A \rightarrow M \text{ and } M \rightarrow B$$

where A and B respectively denote the initial and final products of the reaction, and M the intermediate products In the reaction just considered, M is represented by MnO_{n+2} Under the prevailing conditions, A does not form B directly Consecutive reactions are those in which intermediate products are produced which do not necessarily appear as final products in the reaction. Consecutive reactions occur in stages, one stage must be in progress before another can start. The speed of formation of B from A obviously depends on the speed of the intermediate reactions. If the reaction $A \rightarrow M$ be very rapid, and $M \rightarrow B$ be very slow, the intermediate product M will accumulate in the system, and could be recognized and probably isolated. Several examples are known On the other hand, if $A \rightarrow M$ be very slow, and $M \rightarrow B$ be very fast, it would be

hopeless to look for intermediate products, and the evidence in support of the assertion that the reaction involves a sequence of consecutive or intermediate reactions must be circumstantial, not direct proof [1]

§ 6 Concurrent or Side Reactions

Attention must be again drawn to the curious way potassium chlorate decomposes when heated (p 129) Part of the chlorate decomposes into potassium chloride and oxygen

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

and part oxidizes another part of the chlorate into potassium perchlorate ($KClO_4$)

$$KClO_3 + 3KClO_3 \rightarrow KCl + 3KClO_4$$

These two reactions proceed side by side—concurrently, yet independently, Measurements of the relative proportions of potassium perchlorate and oxygen formed at different temperatures show that the potassium perchlorate reaction proceeds nearly twice as fast as the other reaction The lower the temperature, the greater the relative speed of the perchlorate reaction Hence as the potassium perchlorate accumulates in the system, the molten mass becomes more and more viscid, and if the temperature be below the melting point of potassium perchlorate (610°), the mass solidifies when enough potassium perchlorate has accumulated in the system, even though the temperature be higher than the melting point of potassium chlorate (340°) When the temperature is raised high enough, the potassium perchlorate decomposes into potassium chloride and free oxygen Here again the opening and closing scenes are represented by the equation

$$KClO_4 = KCl + 2O_2$$

But the whole reaction could perhaps be better represented by the scheme [2]

$$\begin{array}{lllll} & & \text{Between } 340°\text{–}610° & & \text{Above } 610° \\ 6KClO_3 & \nearrow & KCl + 3KClO_4 & \rightarrow & 4KCl + 6O_2 \\ & \searrow & 2KCl + 3O_2 & & \end{array}$$

When two or more reactions proceed simultaneously and independently side by side in the same system they are said to be concurrent or side reactions If one of the reactions proceeds much faster than the others, it is said to be the main reaction , the others, side reactions When potassium chlorate is heated with manganese dioxide, no potassium perchlorate has yet been detected among products of the reaction Hence it is inferred that no potassium perchlorate is formed If this be correct,

[1] It will also be obvious that the same reasoning must apply in a longer series of intermediate reactions, $A \rightarrow M$, $M \rightarrow N$, $N \rightarrow B$, *etc* *Similarly*, one or more of the intermediate reactions might be concurrent reactions (see below), or opposing reactions (p 97)

[2] This view of the mechanism of the decomposition of potassium chlorate by heat shows how the relative proportions of potassium chloride, perchlorate, and oxygen depend on the temperature, and almost an infinite number of equations are possible The students must bear this in mind when reading many text-books, for the reaction is often represented by complex equations It can be shown that all so far proposed are special cases of the simple equations described in the text, and these are based on the work of W H. Sodeau (1900–1903)

the cyclic reactions between the manganese dioxide and potassium chlorate proceed rapidly at a temperature much lower than that at which the perchlorate reaction has acquired an appreciable velocity In fine, the catalytic agent accelerates at least one of the two concurrent reactions.

It must not be supposed that the above outline gives a complete representation of this remarkable reaction The products of the reaction may interact with themselves or with the catalytic reagent. In some cases part of the oxygen comes off as ozone, and the products of the reaction may contain a little chlorine Traces of potassium permanganate have been detected among the residual products The chlorine and potassium permanganate are probably formed by a reaction between the potassium chloride and the manganese dioxide. As soon as the student gets beyond the kindergarten or pyrotechnical stages, chemistry becomes intellectually fascinating

§ 7 The Origin of the Terms Acid, Base, and Salt.

The early chemists appear to have gradually learned to arrange certain ıbstances into two groups according as these substances possessed certain ualities in common with vinegar or with wood ashes The former were ılled acids (from the Latin, *acidus*, acid), and the latter, *alkalies* rom the Arabian, *alkali*, ashes of a plant), because the alkalies were enerally obtained by calcining various materials and reducing them to shes. Towards the end of the seventeenth century, Robert Boyle sumıarized the properties of acids as substances which (1) have a sour taste, 2) dissolve many substances (corrosive), (3) precipitate sulphur from lkaline solutions of sulphur, (4) change many vegetable blue colours *g* blue litmus) red, and (5) lose their acid characteristics when brought ıto contact with the alkalies The alkalies were considered to be sub tances which (1) possessed detergent and soapy properties, (2) dissolved ıls and sulphur, (3) restored vegetable colours reddened by acids, nd (4) had the power of reacting with acids to produce indifferent ubstances.

The properties of acids and alkalies were thus opposed to one another, or when mixed together, the one neutralized the other Salts were con dered to be products of the interaction of acids and alkalies. It was soon ound that some substances with alkaline qualities did not melt nor change hen heated, and were almost insoluble in water—these substances were alled *earths* In 1744, F G Rouelle employed the word *base* to include e earths, alkalies, metallic oxides ("calces"), and all substances which roduce salts by reacting with the acids.

It was soon recognized that many substances could not well be grouped ith the acids and bases although they possessed qualities characteristic f acids or bases. Thus aluminium ammonium sulphate—alum—forms a olution with water which has a sour taste, deprives sodium hydroxide f its alkaline qualities, and turns blue litmus red, copper sulphate reddens lue litmus, sodium carbonate and sodium borate turn red litmus blue, tc Conversely, substances may be grouped as acids and bases, even hough they have no action on litmus, *e g* silicic acid, H_2SiO_3, has no action n blue litmus, and yet it is an acid, similarly copper oxide, CuO, is a ase without action on red litmus.

§ 8 Acids.

In his study of the properties of oxygen, Lavoisier noticed that when certain elements were burnt in oxygen, the resulting oxide forms an acid with water—e g carbon, sulphur, and phosphorus. Hence Lavoisier concluded (1777) that "oxygen is an element common to all acids, and the presence of oxygen constitutes or produces their acidity." Lavoisier considered oxygen to be the essential constituent of all acids The very name *oxygen*, given to this element, was derived from Greek words signifying "the generative principle of acids"—ὀξύς (oxus), sour, and γεννάω (gennao), I produce—because "one of the most general properties of this element is to form acids by combining with many different substances" With increasing knowledge, Lavoisier's oxygen theory of acids led to confusion and error, and it was gradually abandoned by chemists when it was recognized that

1. *Some oxides form alkalies, not acids, with water*.—E g sodium, potassium, and calcium oxides As Humphry Davy expressed it, "the principle of acidity of the French nomenclature might now likewise be called the principle of alkalescence"

2 *Some acids do not contain oxygen*.—C L Berthollet showed, in 1787, that hydrocyanic (prussic) acid is a compound of carbon, nitrogen, and hydrogen, but contains no oxygen , and he also came to a similar conclusion with regard to hydro-sulphuric acid—hydrogen sulphide But for some time Lavoisier's reputation had more weight than Berthollet's facts In 1810–11, Humphry Davy proved that hydrochloric acid is a compound of hydrogen and chlorine, and that no oxygen could be detected in the compound. In 1813 Davy also proved that hydriodic acid contained hydrogen and iodine, but no oxygen Hence, added Davy, "acidity is not connected with the presence of any one element"

As a result of Davy's work, the acids came to be classed as hydracids—acids containing no oxygen, and oxyacids—acids formed from acidic oxides In 1815 Davy suggested the possibility that hydrogen, not oxygen, gives the acid characters to the acids, but he did not rush to the other extreme and say that all hydrogen compounds are necessarily acids There is no one property which we can use as an absolute criterion or decisive test of acidity In a crude sort of way, it can be said that *acids usually have a sour taste, are usually corrosive, redden the blue colour of vegetable substances (e.g , litmus), and contain hydrogen, part or all of which can be replaced when the acid is treated with a metal, metallic oxide, hydroxide, or carbonate* Alum, as indicated above, does not contain replaceable hydrogen, and it would not therefore be classed as an acid, although it is sour, corrosive, and colours blue litmus red But we are far from a satisfactory definition of acids, although, as we shall see, we can make a fair definition in terms of the ionic hypothesis [1] Sodium bisulphate has a sour taste, is corrosive, reddens blue litmus, and contains replaceable hydrogen, but it is not usually regarded as an acid because of its mode of formation Naturally the student delights in clear, sharp cut definitions, and teachers of science have many temptations to frame definitions and

[1] Although the definitions in terms of the ionic hypothesis are not very different from the definitions in the text, so far as practical applications are concerned

draw boundary lines which do not exist in nature "Definitions," said John Hunter, "are the most accursed of all things on the face of the earth"

§ 9 Salts

A salt is produced by replacing all or part of the hydrogen of an acid by a metal or basic radicle For instance, zinc displaces the hydrogen of sulphuric acid $Zn + H_2SO_4 = ZnSO_4 + H_2$ forming zinc sulphate as indicated on p 92 Hence C Gerhardt (1843) defined acids to be "salts of hydrogen"

SO_4—Bivalent Radicle		Cl—Univalent Radicle	
Hydrogen sulphate (sulphuric acid)	H_2SO_4	Hydrogen chloride (hydrochloric acid)	HCl
Zinc sulphate	$ZnSO_4$	Zinc chloride	$ZnCl_2$
Sodium sulphate	Na_2SO_4	Sodium chloride	$NaCl$

Salts of the binary acids (*i e.* acids compounded of two elements[1] like hydrochloric acid, hydrofluoric acid, etc) are usually named by dropping the prefix "hydro" and changing the termination "-ic" into "ide" Thus the acids just named furnish chlorides, fluorides, etc To show what chlorides, etc, are in question, the name of the corresponding element (or elements) is introduced as an adjective Thus we have sodium chloride, potassium chloride, calcium chloride, etc The names of the elements are thus used adjectivally in the same sense that the words "stone," "brick," and "wood" prefixed to "house" are adjectival, and indicate the kind of house in question[2]

The salts of the ternary acids (*i e.* acids with three elements) are named by changing the "ic" termination of the acid into "ate," or the "ous" termination of the acid into "ite," and adding the word so obtained to the base or bases forming the salt Thus sulphuric acid forms sulphates—*e g* sodium sulphate, nitric acid, nitrates—*e.g.* calcium nitrate, sulphurous acid, sulphites—*e g* ammonium sulphite, perchloric acid, perchlorates—*e g* potassium perchlorate, hypochlorous acid, hypochlorites—calcium hypochlorite, carbonic acid, carbonates—*e g* calcium carbonate, etc

In normal salts all the displaceable hydrogen of the acid is replaced by the base For instance, sodium sulphate—Na_2SO_4—is a normal salt because all the replaceable hydrogen of sulphuric acid is displaced by sodium In acid salts only part of the replaceable hydrogen has been displaced by a base, and the salt still contains replaceable hydrogen For instance, acid sodium sulphate—$NaHSO_4$—contains half the replaceable hydrogen of sulphuric acid, and half as many equivalents of sodium as normal sodium sulphate If an acid contains two or more replaceable hydrogen atoms, it does not follow that all need be displaced by the same element. These ideas can be illustrated graphically—sulphur sexivalent

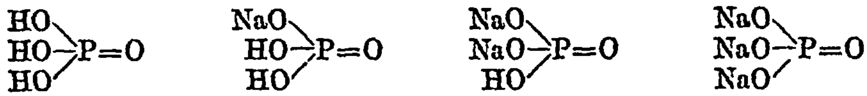
$\begin{matrix}HO\\HO\end{matrix}>S\ll\begin{matrix}O\\O\end{matrix}$	$\begin{matrix}NaO\\HO\end{matrix}>S\ll\begin{matrix}O\\O\end{matrix}$	$\begin{matrix}NaO\\NaO\end{matrix}>S\ll\begin{matrix}O\\O\end{matrix}$	$\begin{matrix}NaO\\KO\end{matrix}>S\ll\begin{matrix}O\\O\end{matrix}$
Sulphuric acid	Acid sodium sulphate	Normal sodium sulphate	Sodium potassium sulphate

[1] Some radicles free from oxygen, *e g* CN or Cy, are regarded as if they were single elements Thus hydrocyanic acid—HCN—furnishes cyanides

[2] Hence, some years ago, the name of the basic element used to be modified

Sometimes the term "hydrogen" is used in place of "acid" for the acid salts, and sometimes the prefix "bi-" or "di-" is appended to the term for the acid in the salt Thus "acid sodium sulphate" is also called "sodium hydrogen sulphate," "sodium bisulphate," as well as "mono-sodium sulphate," etc The normal salts are sometimes called "neutral salts" in the sense that all the hydrogen has been "neutralized" or displaced from the acid These salts, however, are *not* necessarily neutral to litmus—thus normal zinc or copper sulphates react towards litmus as if they were acids, borax, sodium nitrite, and normal sodium carbonate react as if they were alkalies[1] Many acid salts are acid to litmus, *e g* sodium hydrogen sulphate, others are alkaline, *e.g* sodium hydrogen carbonate, others again are neutral, *e g* disodium hydrogen phosphate

It is sometimes necessary to use the prefixes mono-, di-, tri-, . . to discriminate between the different salts of one acid Thus with phosphoric acid—phosphorus quinquevalent—



Phosphoric acid | Monosodium phosphate. | Disodium phosphate | Normal or tri sodium phosphate

It would be a mistake to assume that all the hydrogen of an acid is replaceable by a base Thus, so far as we know, hypophosphorous acid—H_3PO_2—has only one of its three hydrogen atoms replaceable by a metal No one has ever prepared Na_2HPO_2, or Na_3PO_2 The number of atoms of hydrogen in one molecule of an acid which are replaceable by a metal, or a radicle, is termed the basicity of the acid Thus hydrochloric acid—HCl—is monobasic because each molecule of hydrochloric acid contains one replaceable hydrogen atom, sulphuric acid—H_2SO_4—is dibasic, phosphoric acid—H_3PO_4—is tribasic, and silicic acid—H_4SiO_4—is tetrabasic Hypophosphorous acid—H_3PO_2—is monobasic

§ 10 Neutralization

A solution of sulphuric acid, like other acids, colours blue litmus red; and a solution of sodium hydroxide, like other alkalies, colours red litmus blue It is possible to mix the acid with the alkali so as to furnish a solution which neither tastes like sulphuric acid nor like sodium hydroxide The mixture on evaporation furnishes a crystalline solid which neither colours blue litmus red, nor red litmus blue The product of the reaction is said to be neutral, and the process of neutralization consists in adding an acid to an alkali, or of an alkali to an acid, until a neutral substance is obtained The result of the reaction is called a salt. The salt contains the metal of the base, and the radicle or the acid The litmus used to

to give it an adjectival form, hydric chloride, potassic chloride, calcic chloride; etc This system has been abandoned unless it is desired to distinguish between "-ous" and "-ic" compounds—*e g* ferrous chloride, and ferric chloride, etc

[1] Usually mercurous, mercuric, cupric, aluminium, chromic, ferric, stannous stannic, antimonious, and bismuthous salts with the common acids have an acid reaction—redden blue litmus, while the borates, carbonates, chromates, hypochlorites, nitrites, phosphates, silicates, sulphides, and sulphites have an alkaline reaction—turn red litmus blue

determine the point of neutralization is called an indicator Several other indicators besides litmus are available, e g phenolphthalein furnishes a pink coloration with alkaline solutions, and is colourless with acids and neutral solutions, methyl orange is yellow with alkalies, pink with acid and orange with neutral solutions It will be observed that the determination of the neutral point is here referred *arbitrarily* to the behaviour of litmus

Richter's work —The above experiment coupled with numerous others with different acids and bases have proved that acids and alkalies unite to form salts in constant proportions Many of the early chemists —G Homberg (1699), A. L. Lavoisier (1782), H. Cavendish (1788), T Bergman (1785), C F Wenzel (1777), etc —had a more or less clear idea that a definite weight of a base neutralized a definite amount of a given acid · but J B Richter, in an important study of this subject between 1791 and 1802, demonstrated conclusively that the weights of the various acids which neutralize a certain fixed weight of one of the bases are the same for certain fixed weights of all the bases, and the same numbers hold good for the neutralization of the acids by the bases. This is Richter's law of proportionality Consequently it is possible to assign equivalent numbers to the acids and bases For instance, using modern data and terms

Acids	Equivalent weight	Bases	Equivalent weight
Hydrofluoric acid	20 01	Ammonium hydroxide	35·05
Hydrochloric acid	36 47	Calcium hydroxide	37 06
Sulphuric acid	49·04	Sodium hydroxide	40 01
Nitric acid	63 02	Potassium hydroxide	56 00

A table analogous with this, but with less accurate data, was calculated in 1802 by G E Fischer from J B Richter s data, and this was the first table of equivalent weights published. The weights of the acids in one column represent the amounts required to neutralize the quantity of any of the bases indicated in the other column and conversely, the weights of the bases in the second column represent the amounts required to neutralize the quantity of any one of the acids indicated in the first column. Thus 56 grams of potassium hydroxide will neutralize 20·01 grams of hydrofluoric acid, 36 47 grams of hydrochloric acid, 49·04 grams of sulphuric acid 63·02 grams of nitric acid, etc, and 63·02 grams of nitric acid will neutralize 35·05 grams of ammonium hydroxide, 37 06 grams of calcium hydroxide, etc. Richter mixed up much valuable work with several fantastic hypotheses, and he also "cooked" some of his results so that they represent what he thinks he ought to have obtained rather than what he actually observed. Such a procedure is quite antagonistic to the "spirit of science," and made chemists reasonably sceptical about the accuracy of the whole of Richter's work. It was thought, wrongly as it happens, *falsus in uno, falsus in omnibus* (false in one, false in all) Consequently Richter s generalization did not attract the attention it deserved

It follows as a corollary from Richter's law that when two neutral salt solutions mutually decompose one another, the newly formed products are also neutral, because the amount of base neutralized by a certain weight of one acid is also neutralized by an equivalent weight of

another acid It also follows from Richter's law that if one metal is precipitated by another metal from a neutral salt, the neutrality is maintained Richter's generalization has been styled "the law of proportionality," "the law of equivalent ratios," etc and it is obviously a special case of the law of reciprocal proportions of p 28 discovered a few years later

Neutralization versus hydrolysis —The process of neutralization of a basic hydroxide by an acid is attended by the formation of a salt and water We shall find later that some salts—*e g* zinc sulphate, sodium carbonate potassium cyanide, etc —are partially decomposed—*i e* hydrolyzed—by water into acid and base The action of water on such a salt, or of an acid on such a base is thus an example of an opposing reaction, hydrolysis is opposed to neutralization

$$\underset{\text{Neutralization}\longrightarrow}{H_2SO_4 + Zn(OH)_2} \rightleftharpoons \underset{\longleftarrow\text{Hydrolysis}}{ZnSO_4 + 2H_2O}$$

In some cases, however, the amount of hydrolysis is inappreciable, and the process of neutralization is so complete that it can be employed for measuring the quantity of acid or base in a given solution

Acidimetry and alkalimetry —A standard solution containing a known amount of acid or base per litre is prepared and just sufficient of this solution is added to neutralize a solution of a given base or acid The volume of the standard solution required for the purpose is noted It is possible to calculate the amount of "chemically pure" substances present in the given solution from the volume of the standard solution required for the neutralization A standard solution containing one equivalent weight of the acid or base in grams per litre is called a normal solution, written "N-solution," and a solution containing one-tenth the concentration of a normal solution is called a decinormal solution, written "$\frac{1}{10}$ N-solution" The equivalent weight of a base is that quantity which just completely neutralizes one molecular weight of a monobasic acid, and the equivalent weight of an acid is that quantity which contains unit weight of replaceable hydrogen Thus 36 47 grams of HCl per litre gives a normal solution of hydrochloric acid and 49 04 grams of H_2SO_4 per litre gives a normal solution of sulphuric acid Here the molecular weight of the acid is 98 08, and the acid is dibasic for it contains two replaceable hydrogen atoms; and, by definition

$$\text{Equivalent of acid} = \frac{\text{Molecular weight of acid}}{\text{Basicity of acid}}$$

that is, the equivalent of sulphuric acid is 98 08 ÷ 2 = 49 04 A normal solution of sodium hydroxide contains 40 grams of NaOH per litre and a litre of a normal solution of any acid so far considered will just neutralize a litre of a normal solution of any base

Example —Suppose that a 50 c c burette be charged with a normal solution of sodium hydroxide, and suppose that the amount of HCl in 500 c c of a dilute solution of hydrochloric acid be in question—acidimetry—pipette 50 c c of the acid into a beaker and add a few drops of litmus The alkali solution is run from the burette into the acid in the beaker until the addition of but one more drop of acid is needed to change the red litmus to blue Suppose that 42 c c of the normal sodium hydroxide has been run from the burette The argument runs The neutralization $NaOH + HCl = NaCl + H_2O$ shows that 40 grams of sodium hydroxide corresponds with 36 47 grams of HCl, and 1000 c c of NaOH has 40

grams of sodium hydroxide which is equivalent to 36 47 grams of HCl Consequently 42 c c of the standard sodium hydroxide solution is equivalent to 1 53 grams of HCl per 50 c c of the given acid or 15 3 grams of HCl are present in 500 c.c of the given acid

Similar remarks apply to the determination of alkalies—alkalimetry—by standard solutions of the acids This process of analysis is called *volumetric analysis* in contradistinction to *gravimetric analysis*, which involves several weighings during each determination In volumetric analysis, the substance taken for analysis is either weighed or measured, and the preparation of the stock of standard solution may involve one or two weighings, the stock of standard solution may last a great number of analyses Experimental details are discussed in laboratory text-books

§ 11 Bases

A base—Greek βάσις (basis), a base—is a substance which reacts with an acid to produce a salt and water For instance, zinc oxide reacts with sulphuric acid to produce zinc sulphate and water $ZnO + H_2SO_4 = H_2O + ZnSO_4$ Sodium hydroxide reacts with sulphuric acid to produce sodium sulphate and water $2NaOH + H_2SO_4 = 2H_2O + Na_2SO_4$ The bases include the oxides and the hydroxides of the metals, and certain groups of elements equivalent to a metal For convenience, certain groups of elements like ammonia—NH_3, hydroxylamine—NH_2OH, hydrogen phosphide—PH_3, etc , are called bases, although they form salts by direct addition or combination without the separation of water Thus ammonia and hydrogen chloride form ammonia chloride $NH_3 + HCl = NH_4Cl$

The definition of a base indicated above is highly unsatisfactory because it involves the definition of an acid, and we have just acknowledged that a satisfactory definition of an acid is not yet possible Hence our definition of a base defines the unknown in terms of the unknown—*ignotum per ignotius*

"Alkali" and "base" are not synonymous terms Every alkali is a base, but every base is not an alkali The alkaline oxides form very soluble hydroxides with marked basic properties The oxides of the alkaline earths form sparingly soluble hydroxides with less marked basic properties The other oxides, as a rule, do not react directly with water, and the hydroxides are made indirectly An oxide cannot be classed as acidic or basic unless it can be shown to produce corresponding salts

Peroxides —We have seen how barium oxide, BaO—barium bivalent—when heated under certain conditions forms barium peroxide—BaO_2 The peroxides contain a higher proportion of oxygen than the normal oxides Barium oxide with sulphuric acid forms barium sulphate and water $BaO + H_2SO_4 = BaSO_4 + H_2O$ It is therefore a base Barium peroxide forms barium sulphate, water, and oxygen with sulphuric acid $2BaO_2 + 2H_2SO_4 = 2BaSO_4 + 2H_2O + O_2$. $Ba(SO_4)_2$, not $BaSO_4$, corresponds with barium peroxide Hence, barium peroxide is not a basic oxide In view of barium persulphate $Ba(SO_4)_2$, barium peroxide becomes, by definition, a basic oxide.

Amphoteric oxides —Lead dioxide or peroxide, PbO_2—lead quadrivalent—is a basic oxide because it forms the corresponding salt—$PbCl_4$

—with hydrochloric acids But PbO_2 also forms salts—plumbates—with bases, *e.g* potassium plumbate, $O=Pb=(OK)_2$ Hence, a substance may be both acidic and basic according to circumstances Aluminium hydroxide—aluminium tervalent—is a base, because, when treated with an acid, it forms a salt—aluminium chloride, $AlCl_3$—and water

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O$$

But aluminium hydroxide when treated with a base, say, sodium hydroxide, also forms a salt—sodium aluminate, $Al(ONa)_3$—and water

$$Al(OH)_3 + 3NaOH = Al(ONa)_3 + 3H_2O$$

Hence aluminium hydroxide acts towards an acid like a base, and towards a base like an acid Such oxides can be called intermediate oxides, or amphoteric oxides—from the Greek ἀμφότερος (amphoteros), both Zinc oxide is an intermediate oxide Stannic oxide, $O=Sn=O$—tin quadrivalent—forms stannic sulphate, $SO_4=Sn=SO_4$, and also sodium stannate, $O=Sn=(ONa)_2$, hence, stannic oxide is also an intermediate oxide

Basic salts —On comparing the graphic formulæ of the hydroxides of sodium (univalent), lead (bivalent), and bismuth (tervalent)

Na–OH	$Pb<^{OH}_{OH}$	$Bi\begin{cases}OH\\OH\\OH\end{cases}$
Uniacidic base	Biacidic base	Teracidic base

with the graphic formula for mono-, di-, and tri-basic acids we naturally inquire if the OH or hydroxyl group can be replaced by acid radicles one by one so as to furnish uni-, bi-, and ter-acidic bases In the particular examples just selected, the salts

$Pb<^{OH}_{NO_3}$	$Pb<^{NO_3}_{NO_3}$
Basic lead nitrate	Normal lead nitrate

are known The former is called basic lead nitrate, the latter normal lead nitrate, or simply lead nitrate Similarly, $Bi(OH)_2NO_3$, basic bismuth nitrate is known The basic salts are usually, not always, less soluble in water than the corresponding normal salts

§ 12 Hydroxides and Anhydrides

We have seen that sulphur dioxide and phosphorus pentoxide form acids with water

$$\underbrace{SO_2}_{\text{Sulphur dioxide}} + H_2O = \underbrace{H_2SO_3}_{\text{Sulphurous acid}}; \text{ and } \underbrace{P_2O_5}_{\text{Phosphorus pentoxide}} + 3H_2O = \underbrace{2H_3PO_4}_{\text{Phosphoric acid}}$$

The water in these compounds has completely lost its identity, and it is generally supposed to produce a new class of bodies called hydroxides Every element, excepting fluorine and the argon family, appears to form one or more hydroxides, directly or indirectly The oxides from which the acids are produced do not contain the elements of water They are called anhydrides, or "acid anhydrides"—from the Greek α, without, ὕδωρ (hydor), water Thus SO_2 is not only called sulphur dioxide, but also sulphurous anhydride, and P_2O_5 is not only phosphorus pentoxide, but

phosphoric anhydride An anhydride can be regarded as the residue left when the elements of water are removed from the oxyacids Thus sulphuric acid, less water, gives sulphuric anhydride, SO_3, also called sulphur trioxide, sulphurous acid, less water, gives sulphurous anhydride, SO_2 It is generally supposed that sulphurous anhydride in combining with water forms a compound containing quadrivalent sulphur and two univalent hydroxyl, OH, groups, that is, $SO(OH)_2$ The reaction is symbolized

$$O{=}S{=}O + H{-}OH \rightarrow O{=}S\begin{matrix}<\end{matrix}\begin{matrix}OH\\OH\end{matrix} \text{ (sulphurous acid)}$$

and sulphuric acid is considered to be a compound containing sexivalent sulphur and two hydroxyl groups, $SO_2(OH)_2$. The reaction is symbolized

$$\begin{matrix}O\\O\end{matrix}\!\!\geqslant\!S{=}O + H{-}OH \rightarrow \begin{matrix}O\\O\end{matrix}\!\!\geqslant\!S\begin{matrix}<\end{matrix}\begin{matrix}OH\\OH\end{matrix} \text{ (sulphuric acid)}$$

This subject will be resumed later

Thus an anhydride with water forms an acid, and with a base it forms a salt $ZnO + SO_3 = ZnSO_4$ (zinc sulphate)—Sulphurous acid can also be regarded as sulphurous hydroxide, $SO(OH)_2$, and phosphoric acid —phosphorus quinquevalent—as phosphoric hydroxide, $PO(OH)_3$ The basicity of an acid is generally supposed to correspond with the number of hydroxyl groups it contains The hydrogen of the hydroxyl groups is supposed to be the "displaceable hydrogen" referred to in the definition of acids Monobasic hypophosphorous acid, H_3PO_2, is supposed to be $H_2PO(OH)$, or

$$O{=}P\begin{matrix}\diagup H\\ -H\\ \diagdown OH\end{matrix}$$

The basic oxides are sometimes called "basic anhydrides," and they too form hydroxides with water, *e g* calcium oxide, CaO—calcium bivalent —with water forms calcium hydroxide, $Ca(OH)_2$

$$Ca{=}O + H{-}OH \rightarrow Ca\begin{matrix}<\end{matrix}\begin{matrix}OH\\OH\end{matrix}$$

From this point of view water can be regarded as hydrogen hydroxide, H—OH, analogous with K—OH, potassium hydroxide, and Na—OH, sodium hydroxide Excluding certain carbon compounds, the hydroxides of the non metallic elements are usually acids, and the hydroxides of the metals are usually bases The term "hydroxide" is generally reserved for compounds of the basic oxides with water, and the term "anhydride" is usually reserved for the acid anhydrides

Questions

1 Oxygen is to be obtained from mercuric oxide, or manganese dioxide, or potassium chlorate What is the cheapest method of making oxygen per litre, so far as raw materials are concerned, if 100 grams of mercuric oxide costs *9d* 1 kilo of manganese dioxide, *10d*, and 1 kilo of potassium chlorate costs *1s 3d* ?

2 What is the meaning of the term 'normal salt"? Why is the word 'neutral" no longer used to designate these salts?

3 What volume in litres of oxygen measured at 730 mm and 10° can be obtained from one kilogram of pyrolusite containing 80 per cent of manganese peroxide?—*Edinburgh Univ*

4 The atomic weight of carbon was formerly assumed to be 6, and of oxygen 8 State the grounds upon which these atomic weights have been doubled —*Board of Educ*

5 How do the acid forming oxides (anhydrides) differ from the basic oxides? What is usually the effect of bringing together solutions of these two classes of oxides?—*G H Bailey*

6 Give examples showing that the same oxide may at one time function as the acidic constituent of a salt and at another time as the basic constituent —*G H Bailey*

7 Explain what is meant by a "catalytic agent," taking as illustration the preparation of oxygen from potassium chlorate and manganese dioxide.—*Cape Univ*

8 What do you understand by the term "a salt"? Give examples of normal, acid, and basic salts —*London Univ*

9 Define the following terms, giving examples in each case acid, base, acid oxide, basic oxide, basicity, normal salt, acid salt, basic salt —*Sydney Univ*

10 There are reasons to believe that the equations $2KClO_3 \rightarrow KCl + KClO_4 + O_2$, and $KClO_4 \rightarrow KCl + 2O_2$ do not actually represent the decomposition of potassium chlorate when heated Describe the experiments you would make in order to test the validity of the equation —*New Zealand Univ*

11 The atomic weight of a metal M is 56 An oxide of this metal is found to consist of 53 8 per cent of metal, and 46 2 per cent of oxygen. Calculate the formula of the oxide —*London Univ*

12 A mixture of 5 vols of hydrogen and 3 vols of oxygen is exploded by an electric spark, will any gas remain? If so, how much, and how would you ascertain what it is? Suppose a mixture of 3 vols of hydrogen and 5 vols of oxygen had been used, what difference in the results would that have made?

13 Explain the following terms oxide, hydroxide, and hydrate Give examples of each What do you understand by a peroxide and a suboxide?—*Science and Art Dept*

14 Give the atomicity (valency) of each element in the following compounds HCl, H_2O_2, NH_3, CO_2, SO_2, and SH_2 —*Science and Art Dept*

15 How much potassium chlorate must be heated to yield as much oxygen as would be obtainable from 500 grms of mercuric oxide ($K=39$, $Cl=35\ 5$, $O=16$, $Hg=200$)?—*Board of Educ* When two or more reactions follow in succession, or when two reactions are under comparison, it is not usually necessary to make a separate calculation for each reaction Thus, since $KClO_3 \rightarrow KCl + 3O$, and $3HgO \rightarrow 3Hg + 3O$, it follows that $3HgO$ gives the same amount of oxygen as $KClO_3$ Ansr 94 5 grms

16 Why was oxygen so called? What objections can be urged against the name?—*London Univ*

17 It is sometimes said that chemically a metal can be defined as an element capable of forming a base by union with oxygen Discuss this definition

CHAPTER IX

Water

Molecular weight (vapour) H_2O = 18 016, (liquid) $(H_2O)_n$ = n18 016 Melting point 0° at atmospheric pressure, boiling point, 100° at atmospheric pressure critical temperature, + 358° Specific gravity of ice at 0°, 0 9167, water at 0°, 0 99987 One litre of steam at 100° and normal pressure weighs 0 590 grams

§ 1 Water—Occurrence and Purification

Occurrence.—Water is widely distributed in its three states of aggregation—steam or aqueous vapour, liquid water, and solid ice and snow It has been estimated that three-fourths of the surface materials on the crust of the earth is water Animals and plants contain a large proportion of combined water—*e.g* fish contains the equivalent of about 80 per cent, beef, 60–62 per cent, the human body, 70 per cent, aquatic plants between 95 and 99 per cent, and ordinary land plants, 50–75 per cent A great many rocks contain water—combined and absorbed. Clay, for example, contains up to 14 per cent of combined water

The circulation of water in nature—the water cycle.—All the water on the earth passes through a remarkable cycle of changes The heat of the sun leads to the evaporation of water from the seas, etc, water vapour is only 0.62 times as heavy as an equal volume of air, and consequently it rises into the upper regions of the atmosphere. The temperature of the ascending vapour gradually decreases, and consequently a plane must be reached where *the air is saturated with moisture* The vapour will then condense in the form of fine drops of water—mist or clouds The fine drops coalesce into larger drops Ultimately, the condensed water must descend again to the earth as rain, snow, etc. The wind distributes the vapour The heat given up during the condensation of the vapour is distributed or carried from the hotter regions—where evaporation is fastest—to the colder regions—where the vapour is condensed—thus helping to "stretch" the temperate regions nearer to the poles. The water which is sprayed, as rain, etc, on the surface of the globe, does a certain amount of physical and chemical work On the chemical side water helps in the decomposition and weathering of rocks, and on the physical side, it transports matter in suspension from the higher to the lower levels. The soluble matters ultimately collect in the seas

Thus the water cycle involves (1) evaporation from the oceans, seas, lakes, etc, (2) condensation in the upper regions of the atmosphere as a fine mist of distilled water where it collects as clouds, (3) further condensation is followed by rain, (4) the rain-water percolates through the soil and

ex Longer

collects on an impervious bed of rock to be again forced to the surface, as spring water, by the pressure of the superincumbent layers, and (5) this is collected by the streams and rivers and forwarded to the sea, to commence anew the never ending cycle

Rain-water —Rain, in its journey through the air, dissolves oxygen, carbon dioxide, and nitrogen, as well as ammonia and ammonium nitrate It also carries down dust—organic and inorganic Rain water, particularly if collected near the sea in high winds, contains sodium chloride, and if collected near towns, sulphur compounds—sulphur dioxide and sulphuric acid—derived from the products of combustion of coal When evaporated to dryness, 10,000 parts by weight of rain-water will give about 0 34 parts of solid matter, most of this consisting of sodium chloride and organic matter Rain-water contains in solution about 0 013 per cent of dissolved nitrogen, 0 0064 per cent oxygen, and 0 0013 per cent carbon dioxide The rain which falls at the end of a shower is more pure than that which falls at the beginning, because the atmosphere is washed, so to speak, during the earlier part of the shower

Spring and mineral water —Directly the rain-water strikes the ground, it begins to attack and dissolve various rocks, decaying organic tissue (humic compounds), etc, forming *surface and ground water* It is estimated that between 25 and 40 per cent of the rainfall, in temperate regions, soaks into the ground In its journey underground—*underground water*—the percolating water loses most of its organic matter and dissolves more or less mineral matters—compounds of calcium, magnesium, and sodium, carbon dioxide, etc The greater the depth to which the water sinks the greater the amount of solid matter it can dissolve Water under great pressure is a powerful solvent Sooner or later the water which has percolated underground will be forced to the surface as *spring water* If the spring water holds an unusual amount of some particular constituent in solution which gives it a marked taste, or some specific property, the term *mineral water* is applied Mineral waters do not necessarily contain a large excess of mineral matters in solution The water from mineral springs is often named according to some special constituent "Fresh water" is a vague term applied to a natural water which does not contain much dissolved impurity

Chalybeate waters contain ferrous carbonate—*e g* Tunbridge, Buxton, "Excelsior Spring," Saratoga, N Y, "Hot Springs" of Arkansas, Homberg, etc *Sulphur waters* contain hydrogen sulphide and other sulphur compounds, alkaline sulphides, etc—*e g* Baden, Harrogate, Bath, Aachen, "Red Sulphur Spring," Sharon, N Y, etc The water of the Steamboat Springs in Nevada has borates and deposits a sinter containing arsenic, antimony, mercury, lead and copper sulphides, as well as traces of gold and silver *Saline waters* contain salts of various kinds, for instance, magnesium sulphate and chloride which give the water a bitter taste—*e g* Bath, Epsom, Seidlitz, Friedrichshall, Ofen, Cheltenham, etc *Sodium sulphate and sodium carbonate*—*e g* Marienbad, Carlsbad, etc *Carbon dioxide (acid reaction)*—*e g* Apollinaris (imitations of this and other mineral waters are made artificially, the natural water is bottled and exported) *Carbon dioxide with sodium carbonate (alkaline reaction)*—*e g* Vichy, Neuenahr, etc *Carbon dioxide with sodium carbonate and sodium chloride*—*e g* Ems, Nieder-Selters, etc *Sodium and other chlorides*—*e g* Homburg, Aachen, Baden-Baden, "Congress Spring," Saratoga, N Y, etc *Iodine and bromine compounds*—*e g* "Congress Spring," and "Excelsior Spring," Saratoga, N Y, Woodhall Spa, etc *Arsenic*—*e g* Roncegno, Levico, etc *Lithia*—*e g* "Congress Spring," Saratoga, N Y, etc *Boric acid*—*q v* *Silica*—*q v* *Hard waters* are described under "carbonates" The waters of some springs,

particularly in volcanic districts, issue at an elevated temperature, hence the term *thermal waters*—*e g* "Hot Springs," New Zealand (about 60°), Teplitz (39°-49°), Vichy (32°), San Bernadine, California (40°–78°), etc

River water.—Spring water collects in rivers and streams Rivers contain not only the solid matter furnished by spring waters, but also organic matter derived from plants growing on the sides and bottom of the river, and also from the villages and towns through which the river passes The river, in virtue of its greater volume and force, carries along a considerable amount of suspended solids River water also contains in solution matter from the country which it drains Thus the water of the Dee (Scotland), draining slate and sandstone rocks, contains about 0 0056 per cent of solid matter, about one fourth of this being calcium salts, the Thames, draining chalk rocks, contains about 0 03 per cent of solid matter, two thirds of which is calcium salts.

Sea water.—Just as spring water flows into the rivers, the rivers flow into the sea carrying their dissolved salts, and suspended matters which have not been deposited in transit The vapour which rises from the sea by evaporation is almost pure water, hence, unless the dissolved matters are continuously removed, sea water must be gradually getting more and more "salty" Sea water contains a relatively large proportion of soluble salts [1]—about 3 5 per cent of solids in solution Where the evaporation is greatest we naturally expect to find the greatest proportion of salts in solution Thus the Mediterranean contains about 3 4 per cent of solids in solution, whereas the Baltic, with its numerous tributaries, and less evaporation, contains between 0 3 and 0 8 per cent. of solids in solution Salts accumulate in land-locked seas and lakes much faster than in the sea. In illustration, the Dead Sea contains 22 8 per cent of solids in solution, the Great Salt Lake (Utah), 23 per cent, and the Elton Lake (Russia), 27 per cent. These masses of water behave as if they were exposed in a large evaporating basin, for the salts accumulate in the water and are deposited in crystalline masses on the shores of the lakes as the water evaporates.

Potable and drinking water.—The inorganic or mineral matters usually found in solution in natural water are not directly injurious to health. The purification of water for towns and cities is a very important practical problem for the chemist The best solution can only follow after a careful study of the local conditions. Water should be free from pathogenic (disease producing) bacteria, and from suspended impurities This is generally done by filtration through large filter beds made from layers of sand and gravel extending in some cases over an acre of ground. A Pasteur-Chamberlain's bougie (candle), made of unglazed and porous earthenware, and shaped like a hollow candle, is arranged to be screwed on to the water tap, Fig 49 The water is forced through the earthenware by the pressure of the main. Bacteria, organic matter, etc, collect on the inside of the bougie as a slimy layer which clogs the filter The bougie, Fig 49, must be frequently cleaned or replaced (1) to permit the free passage of water, and (2) to remove the layer of slimy organic matter

[1] For instance, an average type contains about 96 5 per cent of water, 2 7 per cent. of sodium salts, 0 07 per cent of potassium salts, 0 14 per cent of calcium salts, 0 59 per cent of magnesium salts, as well as dissolved gases, 0 012 per cent of nitrogen, 0 006 per cent of oxygen, and 0 017 per cent of carbon dioxide

which serves as a medium for the growth of bacteria. In some cases the bacteria are killed by the addition of minute traces of an oxidizer—ozone, sodium hypochlorite, copper sulphate, etc The salt last named also prevents the growth of green algæ which are sometimes very troublesome

To maintain the purity of the water supply up to the proper standard, it is necessary to make (1) regular bacteriological examinations for pathogenic germs; (2) chemical examinations for nitrogenous organic matter—albumenoids, etc —upon which bacteria feed, and for the products of bacterial life—free ammonia, ammonium nitrate and nitrite The presence of these substances in water throws it under suspicion And (3) a periodical critical examination of the source from which the water is obtained

The distillation of water —Water is purified on a small scale by distillation The water is boiled in a flask or boiler and the steam is condensed back to the liquid condition by passage through a tube about which a continual stream of cold water flows To economize space, the condensing

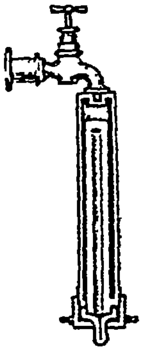


Fig 49.—Filtration by Pressure

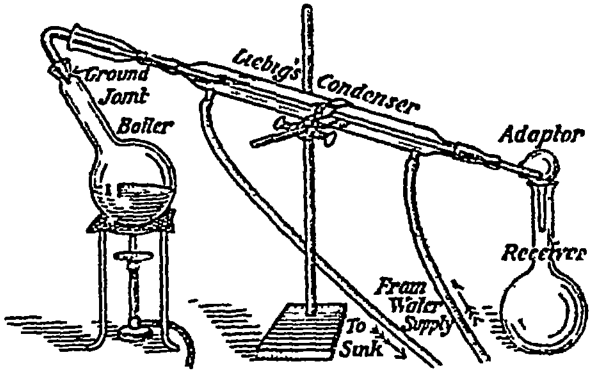


Fig 50 —The Distillation of Water

tube is generally coiled as a spiral—called "the worm"—and kept in a tank through which cold water continually flows Fig 50 represents the form used by T W Richards in some atomic weight determinations It is a modification of that sometimes employed in the laboratory for distilling small quantities of liquid The purpose of Richards' scheme is to prevent the steam coming in contact with rubber or cork stoppers, etc —nothing but glass In place of the "ground joint" a one-hole rubber or cork stopper and glass tube are often used, and in place of the "adapter," the receiver is tilted so that the condenser tube dips into the neck of the flask A small amount of volatile organic matter is usually carried over with the first rush of steam, and soluble matters derived from the glass may be found in the distillate By adding a little potassium permanganate in alkaline solution to the water to be distilled, and rejecting the first portions carried over, fairly pure water can be obtained—particularly if the final product be redistilled in a platinum or gold vessel Block-tin condensers are better than glass, since the water acts very much more vigorously on glass than it does on tin Distilled water which has been kept some time in a glass bottle cannot be used satisfactorily in the analysis of silicates, because it contaminates the silicate undergoing analysis with some of the constituents to be determined.

§ 2 Some Properties of Water

At ordinary temperatures, pure water is a tasteless and odourless liquid, it is colourless in moderately thin layers, but appears greenish-blue when viewed in thick layers. According to Atkins, the blue colour of large bodies of water—*e g* in china clay settling pits in tanks in which water is being softened by the addition of milk of lime, etc.—is an optical effect due to the action of the fine particles suspended in the liquid on the light.

Liquids are but slightly compressible If 1000 c c of water be subjected to a pressure of two atmospheres the volume will be reduced 0 05 c c According to P G Tait, this very small compressibility means that if sea-water were quite incompressible, the average level of the sea would be raised 116 feet higher than it is to day, and 4 per cent. of the present land surface would be submerged

Non metallic liquids are bad conductors of heat, water is one of the best of liquids for conducting heat (mercury excepted), but even then, the thermal conductivity is small Witness, a piece of weighted ice at the bottom of a test-tube of cold water If the test tube be held obliquely, and heated by a Bunsen's burner near the surface, the water at the surface will boil, but the ice at the bottom will remain unmelted.

Water boils at 100° and 760 mm pressure The greater the pressure, the higher the boiling point, and conversely, the less the pressure,[1] the lower the boiling point These phenomena occur with liquids generally, and it is therefore necessary to state the pressure when giving the boiling point of a liquid. Thus at Quito (9350 feet above sea level), with the barometer at an average height, 525 4 mm water boils at 90 1°, and on the top of Mount Everest (29,002 feet), barometer at 255 3 mm, water would boil at 72° Steam or water vapour is an invisible, colourless gas which condenses to a visible cloud of small particles when it comes in contact with the atmosphere This is readily shown by boiling water in a flask, inside the flask, the vapour is invisible, and a cloud of minute water particles—condensed steam—appears where the steam comes in contact with the cold air

Liquid water freezes at 0° into crystalline ice. Water vapour freezes into hoar frost and snow The crystals of ice are extremely rare and difficult to measure. The crystals can often be seen when a piece of ice is examined with a lens while a beam of bright light is passed through it Snow crystals are common They appear in the form of an hexagonal (six-sided) nucleus or six rayed star with the rays developed in bewildering complexity No two seem alike Ice appears to be colourless or white when pure, but it is pale blue when seen in large masses.

By plotting the volume of a given mass of water at different temperatures, we get a curve similar to that illustrated in Fig 51 This curve, at temperatures above 4°, shows that water, like most liquids, expands when heated and contracts when cooled down to 4°, but the curve below 4° is abnormal It shows that water expands when cooled below, and contracts when heated up to 4° If the specific gravity of water at 4° be taken as unity, it follows that water becomes specifically lighter when the temperature is raised or lowered beyond this point The expansion of water

[1] Roughly about $\frac{1}{27}$° C per mm for a few degrees above and below 100°

when cooled from 4° to 0° is very small, but that minute quantity has a very important bearing in nature. When the water on the surface of, say, a lake is cooled, it contracts. The heavier cold water sinks, and the warm water rises. This circulation cools the temperature of the whole body of water down to 4°; any further cooling results in the formation of specifically lighter water. Accordingly, this remains on the surface, and circulation ceases. Finally, as a result of this remarkable and abnormal property, when the temperature of the atmosphere falls to 0°, a surface film of ice is formed.[1] If the water did not expand in this way, as the temperature fell to 0°, the whole body of water would freeze from below upwards and produce profound climatic changes, since the larger amount of ice formed in winter would materially affect the temperature for the rest of the year. In the act of freezing water expands so that 100 c.c. of liquid water at 0° gives approximately 110 c.c. of ice at the same temperature. The specific gravity of ice at 0° varies with its mode of formation from 0.9159 to 0.9182, the specific gravity of water at 0° is 0.999867. Accordingly, ice floats on the surface of water. The expansion of water during freezing is an important factor. The expansion may burst the intercellular tissue of plants by freezing the cell-sap; the expansion may disrupt the fibres of flesh, so that frozen meat appears rather more "pulpy" than ordinary meat. If water freezes in pipes, the expansion of water in the act of freezing may burst the pipe, and water will "leak" when the ice "thaws"; water freezing in the surface crevices of rocks splits and widens the fissures so that the surface crust of the rock appears to disintegrate during a "thaw." The *débris* collects as "talus" at the foot of the rocks, ready to be transported by water to lower levels. Hence this simple force plays an important part in the weathering and decay of rocks, building stones, etc., in countries exposed to alternate frost and thaw, and J. Tyndall adds: "The records of geology are mainly the history of the work of water."

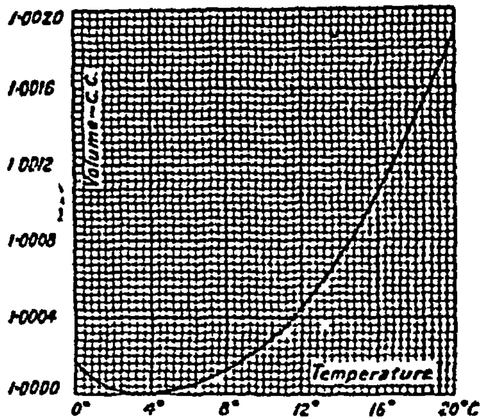


FIG. 51.—Relations between the Volume and Temperature of Water.

§ 3. The Molecular Structure of Water.

Steam or water vapour.—The student so frequently represents water by the formula H_2O, that he soon believes that this symbol correctly represents the molecule of liquid water. As a matter of fact, the molecule of water is probably much more complex. The vapour density of steam is rather too great for the molecular formula H_2O, and much too small for H_4O_2. It is therefore assumed that steam contains a mixture of H_2O with a few H_4O_2 molecules, and that the equilibrium condition for water

[1] "Ground ice" or "anchor ice" is formed at the bottom of rapidly moving streams when the water is thoroughly mixed and does not settle in layers.

vapour, $H_4O_2 \rightleftharpoons 2H_2O$, corresponds with 91 per cent of H_2O molecules in the vicinity of 100°

Liquid water—In order to explain the very curious physical properties of liquid water, *e g* Fig 51, it was assumed by W Röntgen (1891), that water is a mixture of two kinds of molecules which he called "ice molecules" and "water molecules" The "ice molecules" were supposed to form a mass more complex though less dense than "water molecules," so that during the fusion of ice and the subsequent warming of the ice cold water, the volume contracts as indicated in Fig 51 Later investigations have led to the *assumption* that liquid water contains three kinds of molecules which are formed by the association of, say, n simple molecules of H_2O to form more complex molecules, $(H_2O)_n$ There may be some difference of opinion as to the numerical values of n, but there is little room for doubt about the existence of complex molecules The simplest assumptions are that $n = 1, 2$, and 3, so that the three kinds of molecules are represented H_2O, which has been called "hydrol", H_4O_2, called "dihydrol", and H_6O_3, called "trihydrol"[1]

Ice or solid water—G Tammann (1910) has studied the effects of great pressures on the properties of ice, and deduced the existence of two distinct varieties Ordinary ice, which crystallizes in the hexagonal system, and which he calls **Ice I**, or light ice, because it is lighter than water at ordinary temperatures, and **Ice III**, or dense ice, formed by subjecting ice to pressures exceeding 2000 atmospheres, and which passes at once into ordinary "Ice I" if the pressure be reduced The transformation of "Ice III" into "Ice I" can be delayed by reducing the temperature, so that samples can be examined in vessels at the temperature of liquid air, about −180° If ice be made by freezing water while under a pressure between 500 and 2000 atmospheres, a variety of light ice is obtained called **Ice IV**, because it is not quite identical in properties with "Ice I." Similarly, if dense ice be made by freezing water while under a pressure of about 3000 atmospheres, a variety of dense ice—called **Ice II**—is obtained which is not the same as "Ice III," made by compressing ice itself to 3000 atmospheres "Ice III" is stable below 33 4° at 2220 atm pressure, and below −26° at 3116 atm. pressure A fifth variety, **Ice V**, has been prepared at −17° under a pressure of 3420 atm. This passes into a sixth variety, **Ice VI**, at 6170 atm. pressure *Ice VI exists only above 0°C*, and the effect of pressure on its melting point has been traced up to the comparatively high temperature 76 35° at 20,000 atm pressure

If these views about the constitution of steam, liquid water, and ice be correct, it is hardly correct to say, without some reservations, that the passage of ice to liquid water and to steam, and the converse changes, are purely physical changes Confer §§ 2 and 3, Chapter II

[1] In an attempt to account for the properties of dilute solutions, H E Armstrong (1908) further assumed that some of these molecules have the same composition, but a different structure, thus the dihydrol, H_4O_2, molecule is assumed by Armstrong to exist in two different forms

Dihydrone $\begin{matrix}H\\H\end{matrix}{>}O{=}O{<}\begin{matrix}H\\H\end{matrix}$ Hydronol $\begin{matrix}H\\H\end{matrix}{>}O{<}\begin{matrix}OH\\H\end{matrix}$

But this is not the place to discuss the evidence adduced in favour of a belief in the real existence of these imaginary substances

§ 4 The Vapour-pressure of Water Boiling.

Kinetic theory of evaporation—The molecules of a liquid are probably much closer together than is the case with gases, and they are accordingly subjected to the action of comparatively powerful inter-molecular forces Diffusion also shows that the molecules of a liquid are in motion, but, in consequence of the great overcrowding, the number of collisions must be comparatively great The molecules in the body of the liquid are attracted by the other molecules equally in all directions, but at the surface, the molecule can only be attracted inwards. What will happen to a molecule, which, in the course of its wanderings, reaches the surface? If its velocity be great enough the molecule will rush upwards beyond the range of attraction of the other molecules in the liquid, and thus pass into the space above On the other hand, if the velocity of the escaping molecule be not great enough to carry the molecule so far, the upward velocity of the molecule will become less and less, and finally the molecule will fall back and plunge into the liquid again The case is somewhat analogous with the behaviour of a stone thrown into the air If the stone were projected upwards with a sufficient velocity, say 50,000 feet per second, it would leave the earth never to return Hence if the boundary surface of a liquid could be magnified sufficiently, and if the kinetic theory be correct, a cross-section of the liquid would present some such appearance as indicated in Fig 52 (after A D Risteen) The trajectories of the molecules are also shown in the diagram Many of the molecules which leave the surface of the water fall back again, and those which leave and do not return reduce the volume of the liquid, and finally lead to the complete evaporation of the liquid Raising the temperature of the liquid accelerates the motions of the molecules and so hastens the process of evaporation A draught of air across the surface also favours the passage of the molecules away from the atmosphere above the evaporating liquid and reduces the chance of return

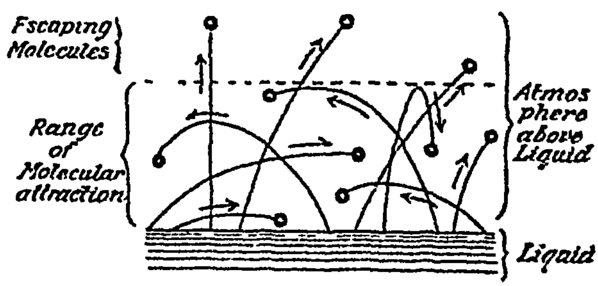


Fig 52—Diagrammatic Representation of the Molecules just above the Surface of an Evaporating Liquid

Cooling effect during evaporation—A liquid becomes cooler during evaporation The kinetic theory shows how this can occur During evaporation, the fleetest molecules can alone escape from the liquid, the more sluggish molecules cannot get beyond the range of attraction of the molecules remaining in the liquid The fleetest molecules have the greatest kinetic energy, and we have seen, p 115, that the temperature of a mass of molecules is proportional to the average kinetic energy of the molecules If, therefore, the fastest molecules escape, the more sluggish molecules will remain behind, and the average velocity of the molecules of the liquid must be reduced Hence a liquid which is evaporating is cooling rapidly. To illustrate the cooling effect of evaporation, a little ether is placed in a

small beaker with a few drops of water on the underside, the water will freeze if the ether be evaporated quickly by blowing a jet of air across the surface. Advantage is taken of this fact to solidify carbon dioxide by the rapid evaporation of liquid carbon dioxide, to solidify hydrogen by the rapid evaporation of liquid hydrogen etc. The principle is also utilized in cold storage, etc.

Heat of evaporation and fusion.—A relatively large amount of energy is needed to transform a gram of water into steam. The thermal energy required has to accelerate the motion of the individual molecules (specific heat) and at the same time to impart to the molecules sufficient momentum to tear them apart against molecular attraction (latent heat of vaporization). The amount of heat required to turn one gram of water at 100° into steam at 100° is 537 cals.[1] This is the latent heat of vaporization of water. The number means that steam at 100° has the equivalent of 537 cals. of energy—internal or potential—more than liquid water at 100°. This energy is degraded as heat when steam at 100° is cooled to liquid water at 100°. Similar remarks might be applied to the melting of ice to liquid water, and the freezing of liquid water into ice. In this case, one gram of ice at 0° in melting to liquid water at 0° requires about 80 cals.—this is the so-called latent heat of fusion. Similar relations hold for other substances. If secondary changes—*e.g.* decomposition during fusion—do not occur all substances exhibit characteristic latent heats of fusion and vaporization. In virtue of these facts, it follows that weight for weight a liquid contains a greater amount of energy than a solid, and a gas contains a greater amount than a liquid. In order to change a solid to a liquid or a liquid into a gas energy must be *added* to the substance and for the converse changes, gas to liquid, or liquid to solid, energy must be *withdrawn* from a substance. The energy needed for the evaporation of natural waters is mainly derived from the "heat paid out by the sun."

Vapour pressure.—Suppose that a liquid is evaporating in a closed vacuous space. The fleetest molecules cannot escape into boundless space, and consequently they accumulate as a gas or vapour in the space above the liquid.[2] The concentration of the vapour in the space above the liquid will go on increasing. The molecules of the vapour behave like the molecules of an ordinary gas, and consequently a certain percentage will plunge back into the liquid. The number of molecules which return to the liquid from the space above per second of course increases as the concentration of the vapour increases, although the rate at which the molecules leave the liquid probably decreases as the concentration of the vapour increases. When the number of molecules which return to the liquid in a given time is equal to the number of molecules which leave the liquid in the same time, the vapour is said to be saturated, and the system in equilibrium. With the notation previously used

$$\text{Water}_{\text{liquid}} \overset{100°}{\rightleftharpoons} \text{Water}_{\text{steam}}$$

[1] A calorie, by the way, is a unit of heat represented by the amount of heat required to raise the temperature of one gram of water one degree.

[2] The distinction between "gas" and "vapour" is somewhat vague. If the "elastic fluid" be very far from its temperature of liquefaction it is generally called a "gas"; and "vapour" if it is near its temperature of liquefaction. *E.g.* oxygen, nitrogen, etc. at ordinary temperatures are gases, whereas water

The equilibrium, it will be observed, is not a static condition, that is, a state of rest. Both processes are active (kinetic), not passive (static). There is a shower of molecules streaming into the liquid, and an efflux of molecules away from the liquid. The effect of one is neutralized by the other; neither can produce any visible result. Anything which disturbs this equality—*e.g.* a desiccating agent or a condenser in the space above (as in distillation, p. 151), etc.—will alter the conditions. Experiment shows that at a given temperature the vapour pressure of a liquid in contact with its own liquid is a constant quantity, and independent of the absolute amount of vapour and of liquid present in the system. It is easy to see this. If the surface of the liquid be doubled, it is true that twice as many molecules will leave the surface in a given time, but twice as many molecules will return.

The vapour pressure of water at 0° is just equal to 4.60 mm. of mercury. This means that if a little water be introduced into the Torricellian vacuum of a barometer, at 0°, the mercury will be depressed from 760 mm. to 755.4 mm. The higher the temperature, the greater the vapour pressure provided all the water is not vaporized; but for any assigned temperature the vapour pressure of a given liquid always has one fixed and definite value. The effect of temperature on the vapour pressure of water is indicated by the curve, Fig. 53, which shows incidentally the effect of introducing a thin layer of liquid water into the Torricellian vacuum; the diagram shows the height of the barometer at different temperatures. The vertical distances between the two dotted curves represent the vapour pressures of water at the corresponding temperatures.

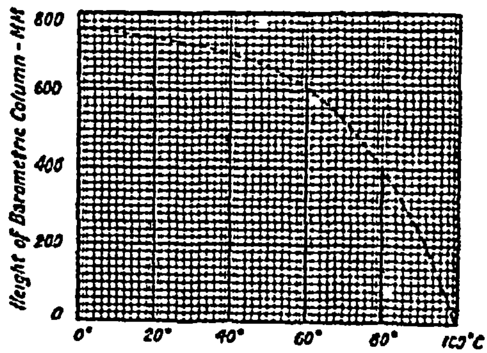


FIG. 53.—Vapour Pressure of Water.

Boiling or ebullition.—As we have just seen, raising the temperature of an evaporating liquid increases the average speed of the molecules, and favours rapid evaporation. When the temperature is high enough, the exposed surface of the liquid is not sufficient to allow the swift-moving molecules to escape fast enough; bubbles of vapour are accordingly formed *within* the liquid. Each bubble as it forms rises to the surface—increasing in size as it rises—and finally escapes into the atmosphere. The process of vaporization by bubble formation is called boiling; and the temperature at which boiling commences, the boiling point of the liquid. When the vapour pressure of the liquid is the same as the external pressure to which the liquid is subjected, the temperature does not usually rise any higher. Increasing the supply of heat increases the rate at which the bubbles are formed. Hence it is sometimes convenient to define: The boiling point of a liquid is the temperature at which the vapour pressure of the liquid is equal to the external pressure exerted at

or alcohol on evaporation would furnish vapours. Otherwise expressed, *a gas is an elastic fluid at a temperature above its critical temperature, and a vapour is an elastic fluid below its critical temperature, but not in a liquid state.*

any point on the liquid surface This external pressure may be exerted by the atmospheric air, by vapour and air, by other gases, etc Hence a table of the vapour pressures of a liquid at different temperatures also shows the boiling points of that liquid under different pressures Thus water at a pressure of 4 6 mm of mercury boils at 0° Hence liquids which decompose at their boiling point under ordinary atmospheric pressure can frequently be distilled without decomposition at the lower boiling temperature obtained by reducing the pressure Hydrogen peroxide can be cited in illustration Hence the so called process of distillation under reduced pressure, or, as it is sometimes less accurately styled, distillation in vacuo The process is illustrated later, Fig 78

Measuring the volume of moist gases—We have discussed evaporation in an evacuated space In 1802 John Dalton showed that *the mass of vapour required to saturate a given space at a given temperature, and consequently also the vapour pressure of a given liquid, is the same whether the vapour be by itself, or associated with other gases upon which it has no chemical action* In other words, the total pressure of a mixture of gas and vapour is the sum of the partial pressures of each constituent When a gas is confined over water, the observed volume of the gas is determined by the temperature and pressure of the barometer By Dalton's law the total pressure of the gas is the joint effect of two partial pressures (1) the partial pressure of the water vapour at the observed temperature, and (2) the partial pressure of the gas under observation Hence the barometer reading does not represent the pressure of the gas, but rather the pressure of the gas plus the pressure of the water vapour To find the latter, note the temperature, and a "Table of Vapour Pressures of Water in Millimetres of Mercury," in most "Table Books," will furnish the desired datum This must be subtracted from the observed pressure (barometer) in order to find the pressure of the gas at the temperature in question

EXAMPLE —What is the volume of 4½ litres of a gas at 0°, 760 mm when it is measured in contact with water at 15°, and the barometer reads 767 7 mm ? From the "Table of Vapour Pressures," the vapour pressure of water at 15° is 12 7 mm Hence the gas is really under a partial pressure of 767 − 12 7 = 755 mm of mercury The problem is now to be solved like the example on p 85 The answer is 4 24 litres

§ 5 The Solubility of Solids

Water is one of the most active of solvents, and, in consequence, it has been styled "the universal solvent," but not in the same sense as the visionaries *alcahest* (universal solvent) so often mentioned in mediæval alchemy For convenience the dissolved substance is often called the solute, and the liquid in which the solute is dissolved the solvent. If potassium chloride be added to water kept at a constant temperature, the salt is gradually dissolved, and the process of solution continues until a definite amount has dissolved The amount of solid remaining in excess of this will remain an indefinite time without further change, provided the temperature remains constant, and no solvent is lost by evaporation The solid and solution are then in equilibrium As in the analogous case of the vapour pressure of a liquid, the equilibrium between a saturated solution and a solid is dynamic, not static Accordingly,

with the preceding notation the equilibria respectively with solid and liquid solutes are represented

$$\text{Solute}_{\text{solid}} \rightleftharpoons \text{Solute}_{\text{sol}}, \text{ or } \text{Solute}_{\text{liq}} \rightleftharpoons \text{Solute}_{\text{sol}}$$

The solution is said to be saturated with the salt at the temperature of experiment. **The weight of salt dissolved by 100 c.c. of the solvent so as to make a saturated solution at any assigned temperature is called the solubility of the salt.**[1] Thus, 100 c.c. of water at 20° will dissolve 35 grams of potassium chloride, and accordingly, 35 is the solubility of potassium chloride in water at 20°. The concentration of a solution is determined by the relative amount of solute in solution. If but a small proportion is present, the solution is said to be *weak* or *dilute*, if a relatively large amount of solute is dissolved, the solution is said to be *strong* or *concentrated*.

The so called insoluble substances obtained as precipitates in analysis are in reality substances with a very low solubility. It is all a question of measurement. As the methods of observation become more and more precise, so does the list of insoluble substances grow less and less. The general use of the term "insoluble" must in consequence give way to "sparingly soluble". In illustration, the three precipitates obtained in the first group of the regular scheme for qualitative analysis are not really insoluble in water because their solubilities, per 100 c.c. of water, at 20°, are represented by the following numbers: silver chloride, 0.00016 gram; mercurous chloride, 0.00031 gram; and lead chloride, 1.18 gram.

The influence of temperature.—The solubility of most substances increases with the temperature; the higher the temperature, the greater the solubility. The relation between the solubility of solids and temperature is usually plotted in the form of curves called **solubility curves**. The solubility curve presents a graphic picture which enables the relation between solubility and temperature to be seen at a glance. In illustration, Fig. 178 shows the solubility curves of potassium and sodium nitrates; Fig. 60 shows solubility curves of potassium chloride, chlorate, and perchlorate. The upward left-to-right slope of the curve shows that the solubility of these salts *increases* with a rise of temperature. Sodium chloride is but slightly more soluble in hot than in cold water, and a few substances give solubility curves with a right-to-left upward slope, showing that the solubility *decreases* with rising temperatures. For instance, see the curve *OB*, Fig. 54, for the solubility of anhydrous sodium sulphate; and also

SOLUBILITY OF	0°	50°	100°
Calcium chromate—$CaCrO_4$	4.50	1.12	0.42
Calcium hydroxide—$Ca(OH)_2$	0.14	0.10	0.06
Cerium sulphate—$Ce_2(SO_4)_3$	19.09	4.78	0.78
Sodium chloride—$NaCl$	35.63	36.67	39.12

Some solubility curves exhibit irregularities at certain temperatures. The solubility curve may change its direction, as calcium sulphate does at 35°, and barium butyrate at 45°. The solubility curve of sodium sulphate is a very trite illustration, but none the less instructive on that account.

[1] Other modes of representing solubility are more convenient in special cases—*e.g.* in Fig. 54 the percentage amount of salt in a given weight of the solution is employed; the volume of gas at n.p.t. per 100 volumes of solvent is used on p. 674, etc.

It is shown in Fig 54 [1] The solubility of the salt, $Na_2SO_4\,10H_2O$, *increases* rapidly with rise of temperature, as shown by the slope of the curve *AO*, Fig 54. There is an abrupt change in the direction of the solubility curve at 33°—*O*, Fig 54 Above that temperature the solubility *decreases* with rise of temperature The interpretation is that the solubility curve is really compounded of two solubility curves. The curve of increasing solubility with rise of temperature below 33° represents the solubility of curve of the decahydrate, $Na_2SO_4\,10H_2O$, and the curve of decreasing solubility with rise of temperature represents the solubility curve of the anhydrous salt, Na_2SO_4 The decahydrate, at 33°, is transformed into the anhydrous salt The decahydrate is not stable above 33°, the anhydrous salt is not stable below 33° This temperature is called the **transition temperature** or **transition point**, and the change is symbolized

$$Na_2SO_4\,10H_2O \overset{33^\circ}{\rightleftarrows} Na_2SO_4 + 10H_2O$$

The solubility curves, it will be observed, represent the condition of equilibrium between the solvent and salt

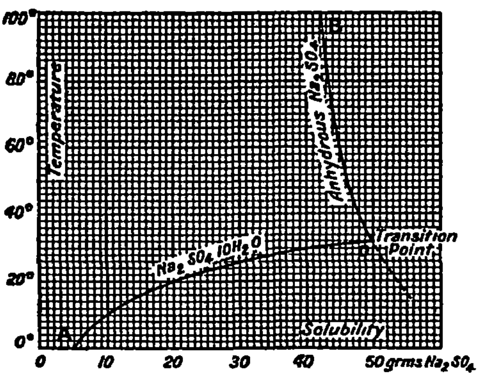


Fig 54 —Solubility Curve of Sodium Sulphate

It makes no difference whether we start with the anhydrous sulphate or the decahydrate When in equilibrium, the solution in contact with the solid will contain the amounts of sodium sulphate—Na_2SO_4—indicated by the solubility curves, Fig 54 The saturated solutions, when in equilibrium, have the same concentration and are identical in every way We cannot continue the observation of the solubility of the decahydrate beyond 32 4° because it *immediately* splits up either into the anhydrous form, or into some less hydrated form—*e g* $Na_2SO_4\,7H_2O$, but since the transformation of the anhydrous salt into the hydrate takes an appreciable time, it is possible to measure the solubility of the anhydrous salt below 32 4. This is indicated by the dotted line in the diagram

The solubilities of the two sodium sulphates—anhydrous and decahydrate—are quite different. If the solid decahydrate were in contact with a saturated solution at 20°, and some of the anhydrous sulphate were added to the solution, some of the anhydrous sulphate would dissolve and be deposited later as the decahydrate The final result would be a transformation, through the medium of the solution, of the anhydrous salt into the decahydrate Although 100 c c of water at 0° can only dissolve about 5 0 grams of the decahydrate, the same quantity of water can dissolve

[1] The ordinates and abscissæ in this diagram are usually reversed It really makes no difference, but for the sake of ease I prefer the system used in the text since we can then see the relation between solubility curves and temperature, concentration diagrams usually represented as in Fig 55

much more of the anhydrous sulphate It is therefore necessary to specify which sodium sulphate is in question when reference is made to "a saturated solution of sodium sulphate"

§ 6 The Freezing of Solutions.

The curve *OB*, Fig 55 represents the solubility of sodium chloride at temperatures ranging from −23° to +40°, the observation cannot be continued below −23° because the whole mass freezes, the upward curve would probably stop only at the melting point of sodium chloride, 801°, if it were not for the volatilization of the water Hence to determine the solubility, the pressure would have to be very great at this high temperature to prevent the water volatilizing

The freezing temperature of a solution is generally lower than that of the pure solvent More than a century ago, C Blagden (1788) cited a number of observations which led him to the belief that the lowering of the freezing point is proportional to the amount of substance in solution In Blagden's own words The effect of a salt is to depress the freezing point in the simple ratio of its proportion to water This generalization is sometimes called Blagden's law The freezing point of an aqueous solution of sodium chloride, that is, the temperature at which *ice* begins to separate, is gradually reduced by the continued addition of small quantities of sodium chloride, and reaches its lowest value, −23°, when the solution has nearly 23 6 per cent of sodium chloride, further additions of the salt raise the temperature at which solid separates *Solid sodium chloride*, not ice, then separates from the solution F Guthrie's measurements (1875) of the relation between the freezing point and the concentration of aqueous solutions of sodium chloride are shown graphically by the curve *AO*, Fig 55

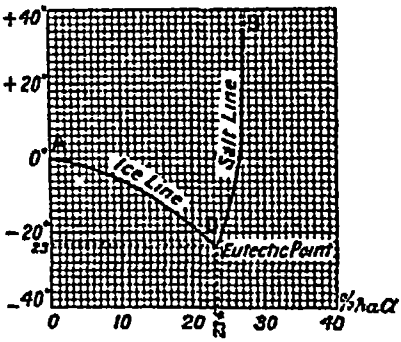


Fig 55—Solubility and Freezing Curves of Sodium Chloride Water Solutions

It has long been known, even as far back as Aristotle's day, that drinkable water could be obtained from frozen sea water, and that if an aqueous solution of salt be gradually cooled, comparatively pure ice first separates from the solution Imagine a 5 per cent solution of salt subjected to a gradually diminishing temperature Start at 0° When the temperature reaches, say, −3 4° ice separates from the solution The mother liquid remaining has therefore more than 5 per cent of salt in solution, as the temperature falls, more ice separates The further concentration of the mother liquid and the separation of ice continue until the mother liquid has about 23 6 per cent of salt, when the whole remaining liquid freezes *en bloc* at −23° Quite an analogous sequence of changes occurs if solutions containing more than 23 6 per cent of salt be gradually cooled This time, however, instead of pure ice, pure salt separates until the residual liquid has 23 6 per cent of salt The whole solidifies *en masse* at −23° If the cooling solution has just 23 6 per cent

of salt, neither ice nor salt separates, until the temperature has fallen to $-23°$, when the whole freezes to a solid mass No other mixture of water and salt freezes at a lower temperature than this Hence a solution containing 23 6 per cent of salt is called a eutectic mixture,[1] and $-23°$ the eutectic temperature. F Guthrie used to think that this mixture—water with 23 6 per cent of salt—corresponded with the formation of a definite compound of sodium chloride and water—$NaCl\ 10H_2O$—stable only at low temperatures Hence his designation cryohydrate for the alleged compound. Ponsot called the substance a cryosel The term "eutectic mixture" is preferred in place of cryohydrate or cryosel

Cryohydrates—We now know that Guthrie's cryohydrates are nothing but mechanical mixtures of ice and salt. The one is entangled with the other It is easy to understand how eutectic mixtures were mistaken for true chemical compounds No matter what the original composition of the salt solution, the last fraction to solidify always has the same composition, and a constant melting point Both these qualities are often stated to be characteristics of true chemical compounds. That the cryohydrates of sodium chloride and numerous other salts are not chemical compounds is based on the following evidence (1) The heterogeneous structure is frequently apparent under the microscope The crystals of ice can often be seen lying in a matrix of salt, especially if a coloured salt like potassium permanganate, copper sulphate, or potassium dichromate be employed. See Fig 177 for an illustration with solutions of carbon in iron (2) Unlike true crystalline compounds, the cryohydrates are generally opaque and ill defined (3) Alcohol may dissolve the solvent leaving behind a network of salt (4) There are no special signs of chemical change during the formation of the cryohydrate (5) The ratio of salt to solvent is not always in molecular proportions. The agreement in some cases is merely a coincidence (6) The composition of a cryohydrate is different when the solidification takes place under different pressures.

The phenomenon—eutexia—which is illustrated above, has attained great importance in the study of metallic alloys, minerals, and mixed salts. Other examples will appear later

§ 7 Gibbs' Phase Rule.

> The phase rule is one of the most comprehensive generalizations known to man It is of unlimited application, and offers an accurate and ready means of classifying all states of physical and chemical equilibria —W MAYERHOFER.

On plotting the vapour pressure of water in the presence of its own liquid, we get the curve *OQ*, Fig 56, which gives the vapour pressure of water corresponding with any given temperature when the liquid and vapour are in contact, and in equilibrium. Call this the steam line, or vaporization curve The ordinate of *O* represents the vapour pressure of water at 0°, at lower temperatures the water freezes Plot in a similar manner the vapour pressure of ice at different temperatures, and we get the curve *OP*, called the hoar frost line, or the sublimation curve Under these

[1] From the Greek εὖ (eu), easily, and τήκω (teko), I melt Hence "eutectic" means "that which is easily melted" The word εὔτηκτος was used by Aristotle (*Problemata*, 1 50) in the sense of easily soluble or digestible

conditions, there is no intermediate liquid state, vapour condenses at once to a solid, and the solid passes directly into vapour Solid iodine below its melting point 114° also vaporizes without liquefaction, arsenic can only be liquefied by melting the element under pressure, under ordinary conditions, arsenic sublimes without fusion It is found that the effect of pressure on the melting point of ice can be represented by a curve *ON*, Fig 56 The left-to-right downward slope of the curve shows that the melting point of ice[1] is lowered by increasing the pressure Thus the melting point of ice at different pressures, according to W Tammann (1900), is approximately

Pressure	260	490	1100	1790	2020 atm
Melting point	−2°	−4°	−10 11°	−17 6°	−20 50°

and *in vacuo*, ice melts at +0 0075° To emphasize these relations, the curves in the diagram are slightly exaggerated The curve *ON* is called the ice line or fusion curve

Before progressing further in our study, it is convenient to fix special meanings to three terms, component, phase, and degree of freedom or variance

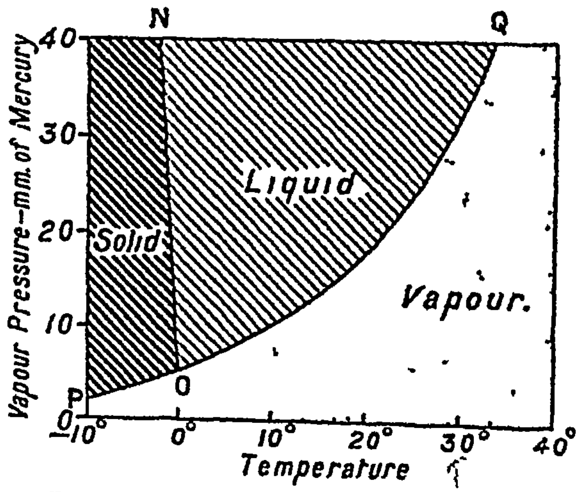


FIG 56 —Vapour Pressure Curves of Water

Components — The components of a system are those substances which take part in the reaction but which are not decomposed in the process The components may be elements, or compounds which behave in a system, for the time being, *as if* they were elements There is only one component in the system just considered, namely, water—H_2O, the components in the system considered in the previous section—an aqueous solution of sodium chloride—are water (H_2O) and sodium chloride (NaCl), and two components were involved in our study of the solubility of sodium sulphate, namely, water (H_2O) and sodium sulphate (Na_2SO_4)

Phases —The components may group themselves in various ways They may pass from one physical state to another, as when water boils or freezes, they may form simple solutions, as when salt dissolves in water, they may combine with one another in various ways, as when sodium sulphate (Na_2SO_4) forms the decahydrate (Na_2SO_4 $10H_2O$), etc Every homogeneous state—solid, liquid, or gaseous—which the components can produce is called a phase The phases of a system are the physical states in which the components can exist A eutectic is not a phase In the case of aqueous solutions of sodium chloride, the eutectic contained two

[1] At very high pressures, ice is said to form at least six different varieties one of which is stable only at temperatures exceeding the melting point, 0° C, of ordinary ice

phases—NaCl and H_2O With an aqueous solution of sodium sulphate at the transition point, Fig 54, we had to deal with four phases—Na_2SO_4, Na_2SO_4 $10H_2O$, the saturated solution, and the vapour arising from the solution With freezing water, we have the three phases ice, water, and vapour In homogeneous systems there can only be one phase, e g gaseous systems, and in heterogeneous systems there are always two or more phases

Variance or degrees of freedom of a system —It will be remembered that the condition of equilibrium of a gas with respect to temperature, pressure, and volume was defined (on p 85) by the equation, $pv = RT$, for R is a numerical constant whose value depends upon the units of measurement (p 78) If only one of these variables be fixed, say the volume, the state of the system will remain undefined, because the gas can retain one fixed volume, and yet have very different values for temperature and pressure Two of the three variables must be known before the state of the system can be defined unequivocally, without ambiguity If any two of the three variables be fixed, the third variable can only assume one definite value The two fixed variables are said to be arbitrary or independent variables, the third variable, which can be calculated from the condition of equilibrium ($pv = RT$) when the two independent variables are known, is called the dependent variable Another term sometimes used for the independent variable is degree of freedom The gaseous system under consideration has two degrees of freedom **The degree of freedom of a system—also called the variance[1] of a system—is the number of independent variables which must be fixed before the state of the system can be defined without ambiguity** The gaseous system defined by the equation, $pv = RT$, is bivariant, because it has two independent variables, or two degrees of freedom

The system consisting of liquid water and vapour has two variables vapour pressure and temperature So long as liquid water is present the pressure is determined solely by its temperature, given either the pressure or the temperature, the other can be determined from the relation symbolized in the vapour pressure curve—Fig 56 Hence the state of the system is defined by two variables—the one is dependent, the other independent. In other words, the system has one degree of freedom, that is, the system is univariant.

The three curves PO, OQ, and ON—Fig 56—represent the conditions of equilibrium of three two phase systems solid-vapour, vapour liquid, and solid liquid respectively These three curves meet at the point O Here three phases can coexist in equilibrium Hence the point O is called a triple point. The co ordinates of the triple point are pressure, 4 57 mm, temperature, 0 0076° C If the pressure or temperature be altered ever so little one of the phases—ice or liquid water—will disappear and a two phase univariant system represented by a point on one of the curves OP, OQ, ON will appear At the triple point the system is invariant. Confining our attention, for the moment, to the liquid and solid, and neglecting the vapour, we can define **The freezing or melting point is the temperature at which both solid and liquid can exist side by side in contact with one another without changing**

Gibbs' phase rule —J W Gibbs (1876–78) discovered an important

[1] That is, "variableness," from the Latin, *variabilis*, variable

relation between the number of components, the phases, and the degrees of freedom of a system According to Gibbs' phase rule, a system will be in equilibrium when its variance is equal to the number of components in the system less the number of phases increased by 2. In symbols

$$F = C - P + 2$$

where C denotes the number of components, P the number of phases, and F the variance or degrees of freedom of the system

Invariant systems —An invariant system has no degrees of freedom, and the state of system cannot therefore survive a change of temperature or pressure In that case $F = 0$, or $P = C + 2$ This means that the system will have $C + 2$ phases if it is in equilibrium If there be one component in the system, as in the case of water at the triple point, three phases can co-exist in equilibrium—ice, liquid water, and steam Otherwise expressed, if a system has three phases and one component the phase rule tells us that it will be invariant, and therefore the slightest alteration of pressure or temperature will cause one of the phases to disappear

Univariant systems —These systems have one degree of freedom, and when the system is in equilibrium, $F = 1$, or $P = C + 1$ If one of the variables be known, the state of the system can be determined as indicated above

Bivariant systems —These systems have two degrees of freedom, and hence $F = 2$, or $P = C$ Two variables must be known before the state of the system can be determined A saturated solution in the presence of an excess of the solute is univariant, but bivariant if not saturated In the former case there are two components and three phases—solid, solution and vapour, in the latter case there are two components and two phases Hence in the one case, $F = 2 + 2 - 3$, and in the other, $F = 2 + 2 - 2$ Again, in the region PON, Fig 56, the system will be bivariant, because there is only one phase and one component Pressure and temperature may be altered without interfering with the state of the aggregation of the ice so long as the variations keep within the boundary lines, PO and ON The same remarks may be applied to the condition of the water represented by points in the regions NOQ and POQ

Object of the phase rule —The phase rule is therefore a method of grouping systems which behave in a similar manner into one class It is essentially a system for the classification of states of equilibrium Systems having the same variance behave in an analogous manner under the influence of variations in temperature, pressure, and volume or concentration It makes no difference whether the changes be chemical or physical As indicated above, the phase rule also tells us whether the phases of a heterogeneous system are those necessary for equilibrium

Special application to solids and liquids —In the application of the phase rule to alloys, minerals, and solutions when the vapour pressure is negligibly small, only two variables need be considered —concentration or volume, and temperature In that case, the phase rule reads.

$$F = C - P + 1$$

Granite, Fig 2—composed of quartz, SiO_2, felspar, $K_2O\ Al_2O_3\ 6SiO_2$, and mica, say, $K_2O\ 3Al_2O_3\ 6SiO_2$—has three components SiO_2, Al_2O_3, and K_2O, and three solid phases mica, quartz, and felspar The system is univariant It is also in equilibrium, because, not being at a

transition point, it is able to survive a small variation of temperature without changing the state of the system

To summarize some of the systems previously considered

TABLE VII.—CLASSIFICATION OF SYSTEMS BY THE PHASE RULE

System	Components	Phases	Degrees of freedom or variance.
Freezing water	Water	Liquid; solid, vapour	Invariant
Water above 0°	Water	Liquid, vapour	Univariant
Unsaturated solution of sodium chloride	Water, salt	Solution; vapour	Bivariant
Saturated solution of sodium sulphate at transition point	Na_2SO_4, H_2O	Na_2SO_4; Na_2SO_4.$10H_2O$, solution, vapour	Invariant
Freezing eutectic—sodium chloride and water	Water, salt	Two solids; one liquid (neglect vapour)	Invariant
Steam and metallic iron in a closed vessel	Iron, oxygen, hydrogen	H_2; H_2O, Fe, Fe_3O_4	Univariant

§ 8 Undercooling—Supersaturation

Undercooling.—Heat a solution of sodium thiosulphate to, say, 70° in a glass flask, stir the molten mass with a thermometer as it cools, read the thermometer every two minutes, and finally plot the results on squared paper A curve—called a *cooling curve*—resembling that illustrated in Fig 57, *A*, will be obtained. The terrace in the cooling curve at 56° shows that a change of some kind takes place in the nature of the cooling substance at 56° The terrace corresponds with the temperature at which solidification or freezing was in active progress The sudden slackening in the rate of cooling corresponds with the "evolution of the latent heat of fusion" as the liquid solidifies Repeat the experiment, but do not agitate the liquid, take care that the cooling liquid is quite still and protected from dust by, say, a loose plug of cotton wool in the neck of the flask A cooling curve like that shown in Fig 57, *B*, will be obtained. The liquid does not freeze, and no abnormal behaviour can be detected in the cooling curve The liquid "ought to"[1] crystallize at 56°, but it does not. Drop a crystal of sodium thiosulphate into the liquid mass The mass seems to solidify with almost explosive rapidity, and the thermometer immediately indicates a rise of temperature The phenomenon is illustrated by Fig 57, *C* The liquid sodium thiosulphate at a temperature below 56° is said to be surfused, or, better, undercooled The liquid may be kept in the surfused

[1] "Ought to" is put in inverted commas to show that the ordinary meaning of these words is modified

or undercooled condition an indefinite time, and the process of solidification can, in general, only be started by the introduction of a crystal of the same type as that which is formed during the solidification of the given substance. Often a fleck of the right kind of dust floating in the air suffices to upset the state of apparent equilibrium Clear glasses and pottery glazes are solutions of silicates which have congealed to hard masses without crystallizing

Supersaturation—Similar phenomena occur if water be saturated with Glauber's salt—$Na_2SO_4 \, 10H_2O$—at 30° Make sure that no excess of solid is in contact with the liquid, and let the solution cool as before—without agitation and without dust The solubility curve, Fig 54, tells us that the solid "ought to" separate from the system as the temperature is reduced Here is another case of apparent, false, or metastable equilibrium Although the solution can be kept an indefinite time in this condition, the seeding, or inoculation, of a supersaturated solution by the introduction of a very minute quantity of a crystal of dissolved salt will upset the state of apparent equilibrium [1] The crystal fragment becomes

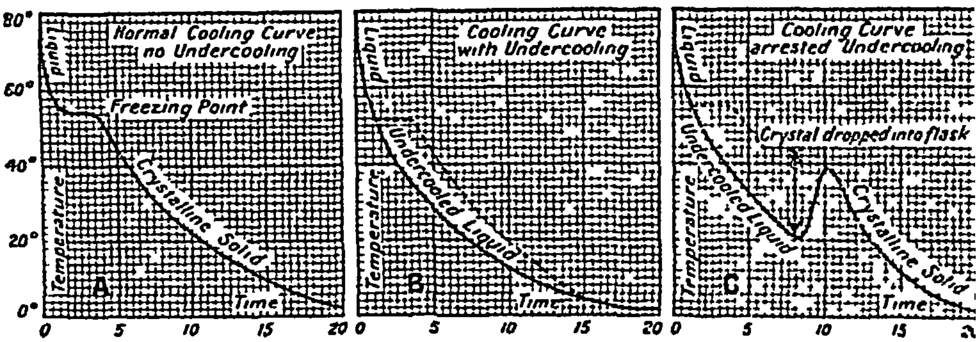


FIG 57—Cooling Curves of Molten Sodium Thiosulphate

the centre or nucleus from which crystals radiate into the solution on all sides Similar results can be obtained with aqueous solutions of sodium acetate, sodium chlorate, etc If a solution holds more salt than corresponds with the normal solubility curve of the salt, the solution is said to be supersaturated

It is possible to distinguish between a saturated, an unsaturated, and a supersaturated solution by bringing each in contact with more of the solid. If the solution is unsaturated, more solid will dissolve, if saturated, none will dissolve, and if supersaturated, solid will separate until the solution is saturated The concentration of an unsaturated solution is less, while the concentration of a supersaturated solution is greater than that of a saturated solution

Related phenomena—Many other examples of related phenomena are known In analytical work the slow appearance of precipitates in dilute solutions is very common Pure water may be easily cooled to $-3°$ or $-4°$

[1] In H. A Miers' experiments on the crystallization of the rare organic compounds, salol and betol, it was found that the substances did not crystallize at first when allowed to cool in open vessels in the laboratory, but after a time, when the air of the laboratory had become impregnated with dust, presumably containing minute grains of both substances, crystallization readily occurred in open vessels exposed in the laboratory

without the appearance of ice if kept quite still while the temperature is reduced, and the water can be easily cooled to $-6°$ or $-7°$ if a layer of oil be placed over the surface of the cooling water Phosphorus, sulphur, etc, behave in a similar manner Ice has not been heated above $0°$ without melting, but liquid water can be heated to 105° or 106° without boiling When the boiling does start, it proceeds with almost explosive violence The phenomenon is called bumping By suspending drops of water in a mixture of olive and linseed oils which has the same specific gravity as water, and a high boiling point, L. Dufour (1863) raised water to 178° without boiling P J Coulier (1875) found that dust free air saturated with moisture may be cooled below the normal temperature of condensation, and John Aitken (1880) showed that dust is necessary for the formation of fogs and raindrops

Metastable and labile states of supersaturation—Inoculation or seeding is usually necessary to start the process of crystallization of a supersaturated solution, and yet the supersaturation may be carried so far that the crystals will grow spontaneously in the solution, without seeding Indeed, it is possible to draw a "supersaturated solubility curve" representing the concentration of a solution at different temperatures where the supersaturation is so great that crystallization will begin spontaneously without inoculation The idea is illustrated in Fig 58, where the region between the normal solubility curve and the supersolubility curve represents what is called the **metastable state** where inoculation is necessary to inaugurate the process of crystallization, and the region beyond this represents the so called **labile state** where crystallization may start spontaneously without inoculation

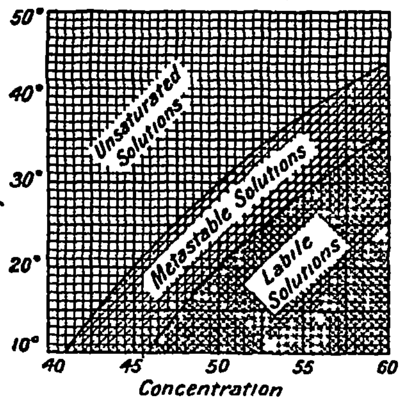


FIG 58—Labile and Metastable Equilibria of Saturated Solutions (after H A Miers)

Supersaturation and the phase rule—The phase rule, it will be observed, applies to systems in real equilibrium, not to systems in a state of apparent, false, or metastable equilibrium We are repeatedly confronted with those little understood phenomena which, for convenience, have been grouped under the general term "passive resistance," p 112

The kinetic theory of supersaturation—The kinetic theory throws a little light on to the phenomenon of supersaturation A saturated solution in contact with the solid is supposed to be closely analogous with a closed vessel containing a liquid in contact with its vapour When in equilibrium, the same number of molecules pass from the surface of the solid into the solution and return from the liquid to the surface of the solid If the state of equilibrium be disturbed by evaporation or by lowering the temperature, the equality of the two opposing actions is disturbed and a new condition of equilibrium is established In the case of a metastable supersaturated solution, the exchange of molecules cannot take place

because no free solid is present Directly a particle of the dissolved solid is added, the dissolved substance is rapidly deposited about the submerged particle as a nucleus until the concentration of the solution has reached its normal value In the case of a labile supersaturated solution, the crowding of the molecules is so great that they are able to form aggregates large enough to serve as nuclei for the separation of more solid

Questions

1 How would you proceed in order to find the volumes in which hydrogen and oxygen combine to form water? What modification of your apparatus would you make, if you were asked, in addition to measure the volume of steam formed? What volume of gas is formed when 72 grams of water are decomposed (a) electrolytically, (b) by means of sodium, (c) by heated iron? [H = 1, O = 16] —*Victoria Univ, Manchester*

2 Write a short account of the physical properties of ice, water, and steam comparing them with those of solids, liquids, and gases in general —*London Univ*

3 How would you prove that the composition of water may be expressed by the formula H_2O? Mention everything that this formula implies What volume would 9 grams of aqueous vapour occupy at 273° C, and under 380 mm pressure? *Aberdeen Univ*

4 The specific gravity of a solution of hydrochloric acid is 1 175, and it contains 34 5 per cent of the compound HCl How many cubic centimetres of the solution will be required for the neutralization of 50 grms of sodium hydroxide, NaOH, given the reaction $HCl + NaOH = H_2O + NaCl$?

5 Give an account of the properties of water, especially those which may be termed chemical properties How would you identify water and distinguish it from other colourless liquids?—*London Univ*

6 Write a short account of the phase rule and indicate clearly some useful applications of this generalization —*Board of Educ.*

7 When ordinary water which has been in contact with the air is boiled, gas is given off How would you collect a sufficient quantity for analyses? How could you prove that the gas was dissolved in water and that it is not a product of the decomposition of water by heat? How would you determine the amount of one of the constituents?—*Oxford Locals*

8 The formula for water has been written at different times HO and H_2O (O = 8) Point out the objections to both expressions and state concisely the reasons for representing the molecule of water by H_2O(O = 16) —*London Univ*

9 Describe some case of chemical combination and some case of solution Compare the two, and discuss the question whether any distinction should or should not be made between solution and other cases of chemical change —*New Zealand Univ*

10 Compare the bubbling of molten potassium chlorate at a high temperature with the bubbling of water when heated to about 100°

11 100 grams of water dissolve the following quantities of zinc sulphate at the temperatures named

Temperature	0°	25°	39°	50°	70°	80°	90°	100°	
$ZnSO_4$	41 9,	57·9,	70 1,	76 8	88 7	86 6,	83 7,	80 8	grams

Plot the results on squared paper so as to show a "solubility curve"

12 Define the terms degree of freedom, phase, component, and variant in Gibbs' rule In the case of a system containing salt and water, and the phases salt, saturated solution, and vapour how many variants must be fixed to establish equilibrium? Discuss the reasons for your statement —*Sydney Univ*

13 Give an account of the phase rule and of the help it affords in understanding equilibria Illustrate your answer in particular by applying the rule to the case of water —*Bombay Univ*

14 Can any distinction be drawn between the action of water on a soluble substance and other cases of chemical combination? What are the resemblances, and what the differences between a substance in dilute solution and the same substance in the gaseous state?—*New Zealand Univ.*

CHAPTER X

CRYSTALS AND CRYSTALLIZATION

§ 1 The Crystallization of Salts from Solutions

IF a saturated solution of a salt be allowed to evaporate, crystals of the salt separate when the concentration of the solution becomes greater than that represented by a point on the solubility curve. The phenomenon becomes a little more complex when the solution contains two or more salts which do not act upon one another

The solubility of a mixture of sodium and potassium chlorides in water at 25° is represented by the curves shown in Fig 59 The ordinates represent quantities of sodium chloride, the abscissæ, quantities of potassium chloride The concentration of a saturated solution of sodium chloride at 25° is represented by the point A, and of a saturated solution of potassium chloride by the point B The line AC represents the composition of solutions of sodium chloride saturated in presence of the proportions of potassium chloride indicated by the abscissæ of the curve AC, and the line CB, the composition of solutions of potassium chloride saturated in presence of the proportions of sodium chloride represented by the ordinates of CB The point C represents the composition of a solution saturated with both salts The volume of solution is here understood to be the amount necessary to dissolve A and B gram molecules of the respective salts

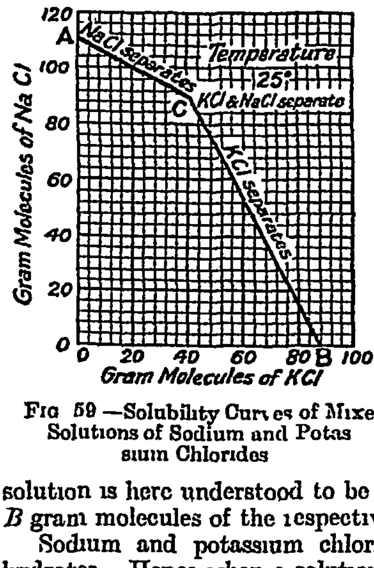


FIG 59 —Solubility Curves of Mixed Solutions of Sodium and Potassium Chlorides

Sodium and potassium chlorides form neither "double salts" nor hydrates Hence when a solution containing equal molecular proportions of both salts is evaporated, the solution will become saturated first with respect to the less soluble potassium chloride, and this salt will accordingly crystallize from the solution first As evaporation proceeds, potassium chloride continues separating, the successive states of the solution are represented by points travelling in the direction BC The phenomenon is really wonderful The molecules of both sodium and potassium chlorides are uniformly diffused throughout the original solution, but, as soon as the evaporating liquid has attained a certain concentration, the molecules of the potassium chloride alone commence crystal building The molecules of this salt withdraw from the solution in harmonious order, which is followed as rigorously as the bricklayer, when building a

mansion, places brick upon brick, according to the plan predetermined by the architect The operation continues until the solution has the composition represented by the point C At C the solution is saturated with respect to both salts Any further concentration of the solution will result in the deposition of sodium and potassium chlorides side by side, and the solution will go on depositing a mixture of the two salts until it has been evaporated to dryness Here the molecules of both salts are simultaneously building crystals side by side If sodium chloride be in excess, what has been said of potassium chloride along BC, applies to sodium chloride along AC In each case C represents *the end point of the crystallization*

§ 2 Fractional Crystallization.

The molecules of a substance in solution appear to be distinct individuals before crystallization, while in a crystallizing solution each molecule appears to exert some specific attraction on its fellow molecules to enable them to separate from the solution in a definite orderly way Warm 50 grams of potassium chlorate, just above its melting point, in a new porcelain dish, and keep the mass at that temperature until it becomes viscid and almost solid This will occupy from ten to fifteen minutes Let the *mass cool It contains* undecomposed potassium chlorate, some potassium chloride, and potassium perchlorate Add 50 c c of hot water, say at 50°, and when all has disintegrated and the solution cooled, the crop of crystals of potassium perchlorate can be filtered off Evaporate the filtrate until a drop crystallizes when rubbed on a cold surface The first crop of crystals which separates is mainly potassium perchlorate, because this salt is so very much less soluble than the other two, 100 c c of water, at 15°, holds in solution about 36 grams of potassium chloride, 6 6 grams of the chlorate, and 1 5 gram of the perchlorate. The solubility curves of these three salts are shown in Fig 60 If the evaporation be carried too far, crystals of potassium chlorate will separate The first crop of crystals is redissolved in hot water and again allowed to crystallize, potassium perchlorate can thus be obtained almost free from the other two salts; and by repeated recrystallization it is possible to isolate the pure salt Recrystallization is needed to get the pure product because the crystallizing salt often carries down with it some of the mother liquid, or some of the other salts dissolved in the mother liquid If the evaporation be continued, potassium chlorate will eventually separate, and the process of recrystallization must be repeated, in order to isolate the pure salt The remaining mother liquid is nearly all potassium chloride

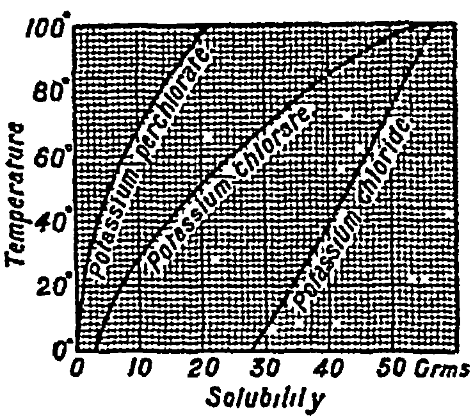


FIG 60 —Solubility Curves of Potassium Chloride, Chlorate, and Perchlorate

This operation—fractional crystallization—is sometimes a useful method of separating salts which differ appreciably in solubility In some

cases it is the only satisfactory method of separation, even though the salts in solution do not differ very much in solubility The process of fractional crystallization is then very laborious, involving, may be, scores of crystallizations and recrystallizations In other cases it is impossible to separate the salts in this way, because double salts separate The microscopic appearance of the three salts isolated in this manner is

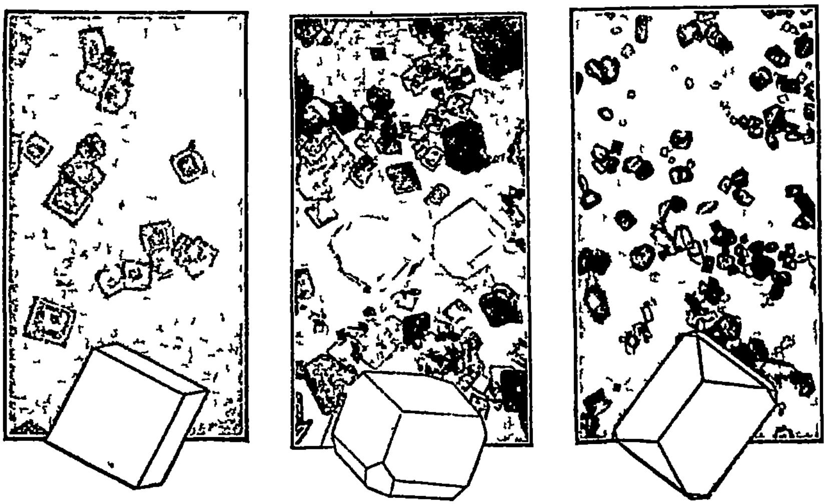


Fig 61 —Crystals of Potassium Chloride, Potassium Chlorate, and Potassium Perchlorate

shown in Fig 61 The outline drawings represent perfect crystals As a rule, the slower the process of crystallization, the larger and more perfect the crystals The crystals are usually more or less distorted because, owing to local differences in the concentration of the crystallizing solution, the solution in the vicinity of some faces of the crystal may be more concentrated than the others Perfect crystals are rarely found in nature or in the laboratory

§ 3 Crystals

> In whatever manner, or under whatever circumstances, a crystal may have been formed, whether in the laboratory of the chemist or in the workshop of nature, in the bodies of animals or in the tissues of plants, up in the sky or in the depths of the earth, whether so rapidly that we may literally see its growth, or by the slow aggregation of its molecules during perhaps hundreds, perhaps thousands of years, we always find that the arrangement of the faces of the crystal, and therefore its other physical properties, are subject to fixed and definite laws.—H P Gurney

The constancy of interfacial angles —When homogeneous substances solidify from a state of vapour, fusion, or solution, their particles cohere so as to form solid figures—crystals—with regular symmetrical shapes bounded by plane faces The solids are then said to be crystallized Every crystalline substance of definite chemical composition has a specific crystalline form characteristic of that substance. This is

sometimes called R J Hauy's law The faces of crystals of the same substance may vary in size and shape, but if the crystals possess the same chemical composition, and are at the same temperature, the *interfacial angles have the same numerical value* In other words, **the angles between similar faces of crystals of the same substance are precisely the same, and are characteristic of that substance** This "law" was first announced by D Guglielmini (1688) This means that the crystalline form of a substance is not determined by the absolute position nor by the sizes of the faces of the crystal, but rather by the dimensions of the interfacial angles

Polymorphism —Crystals of different substances have different forms, crystals of the same substance developed under the same conditions have the same form; but crystals of the same substance developed under different conditions may or may not have the same form For instance, crystals of sulphur formed above or below 94 5°, p 397, there are two differently shaped crystals of sodium phosphate, Fig 62, crystals of sodium chloride are octahedral if grown in alkaline solutions, and cubical in neutral solutions, and conversely, crystals of alum are usually octahedral, but cubical if grown in alkaline solutions Substances which crystallize in two different forms are said to be dimorphous, Fig 62, and substances which crystallize in three different forms are said to be trimorphous Titanic oxide, TiO_2 for example, is known in three forms, rutile, anatase, and brookite *Polymorphism* is the general term applied to the phenomenon when a substance crystallizes in more than one form

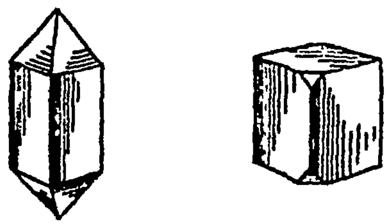


FIG 62 —Dimorphic Forms of Sodium Biphosphate

Ideal and distorted crystals —One or more faces of a crystal may be abnormally developed or stunted in growth During the growth of a crystal, the concentration of the mother liquid is rarely so evenly balanced on all sides as to allow the growth to proceed with the same rapidity in all directions The crystal will grow fastest where the solution is most concentrated If a crystal grows on the bottom of a liquid at rest, flat plates, almost parallel with the bottom of the vessel, may be formed, while if the solution be agitated during crystallization, a more uniform growth in all directions may prevail This is not all, a cubical crystal may habitually grow most rapidly in *one* direction so as to form a needle-like, acicular, or prismatic crystal, *A*, Fig 63 or in *two* directions so as to form a tabular or plate like crystal, *B*, Fig 63, or the crystal may grow uniformly in all *three* directions and the ideal cube, *C*, Fig 63, will be produced The angles between the faces, however will remain unchanged —90° The most suitable condition for uniform growth in all directions occurs when the growing crystal is suspended in the middle of the given solution by means of a thread The crystal then approximates more or less closely

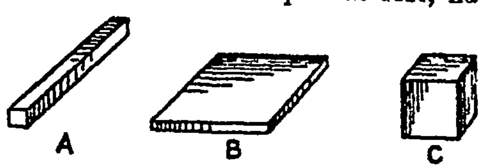


FIG 63 —Ideal and Distorted Crystals.

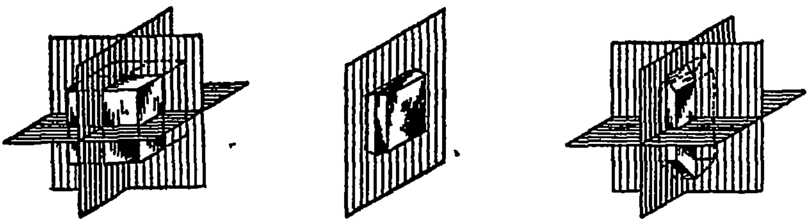
to the ideal form If the crystallization of a solution be rapid, the crystals are usually much smaller than if the process be slow Again, the habit of a crystal may change when grown from liquids containing other salts in solution Thus, potassium chlorate gives prismatic crystals (Fig 61) when grown in aqueous solutions, if much calcium chloride be present, small needle like crystals are obtained, and if potassium iodate be present in the solution, long plate like crystals separate from the solution. The crystal angles, however, are the same in each case

Ideal crystals —However much the crystals may be distorted, the angles between like faces have the same value, and in consequence, similar faces can be imagined at the same distance from the centre of the crystal In this way, the ideal form of a crystal can be derived from that of a distorted crystal

§ 4 The Seven Styles of Crystal Architecture

> A symmetrical shape is one which consists of parts exactly similar, repeated a certain number of times, and placed so as to correspond with each other The symmetrical parts of a crystal are, under like circumstances, alike affected —W WHEWELL.

Planes of symmetry —The great variety of crystals formed by different substances can be arranged into seven systems. Certain qualities are peculiar to the members of each system For instance, the planes of symmetry of each class are characteristic A plane of symmetry is an imaginary plane which divides the crystal into two parts such that one part is the exact but inverse counterpart of the other In other words, the two parts bear to one another the same relation that the image in a mirror bears to its object The mirror is the equivalent of a plane of symmetry A crystal of sodium chloride, for example, has nine planes of symmetry, three are indicated in Fig 64, and six others are obtained by taking planes diagonally through three faces of the cube The crystal of gypsum, Fig 65, has only one plane of symmetry, and a crystal of zinc sulphate has three planes of symmetry, Fig 66 [1]



Planes of Symmetry

FIG 64 —Sodium Chloride FIG 65 —Gypsum FIG 66 —Zinc Sulphate

Axes of symmetry —Then again, a crystal may be rotated about a definite axis through an angle, which is a simple fraction—$\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, or $\frac{1}{6}$ of the angle of complete rotation, 360°—such that the faces, edges, and corners are brought into similar or symmetrical positions, and the aspect of the crystal is the same as before rotation The axes of rotation are then called axes of symmetry. Thus we speak of dyad, triad, tetrad,

[1] Compare also Fig 4 for zinc sulphate

and hexad axes of symmetry according as there are 2, 3, 4, or 6 positions of symmetry during a complete rotation Thus Fig 67, *A*, represents a horizontal cross-section of a crystal with one hexad axis of symmetry, because during the rotation of the crystal about the axis O, there are six positions where the original aspect of the crystal is the same Fig 67, B, C, D, respectively, denote tetrad, triad, and dyad axes of symmetry

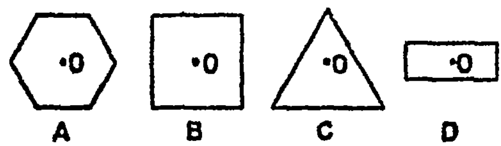


Fig 67 —Axes of Symmetry

Other grades of symmetry, pentad, heptad, octad, etc, are not possible in crystals. The study of the forms of crystals is a special branch of chemical physics—*crystallography* Sufficient is here stated to give the student an idea of a few special terms in common use.

The seven systems of crystal architecture —Every known crystal can be referred to one of the following seven systems :

I Triclinic system —Crystals of this system have no axes nor planes of symmetry This system has also been designated the "anorthic," "clino-rhomboidal," "asymmetric," or the "double oblique" system

EXAMPLES —Potassium dichromate, copper sulphate—$CuSO_4$ $5H_2O$, calcium thiosulphate—CaS_2O_3 $6H_2O$, boric acid, potassium ferricyanide, anhydrous manganese sulphate, copper selenate, anorthite—lime felspar, cryolite, etc

II Monoclinic system —Members of this system have one plane of symmetry, or one dyad axis of symmetry, or both a plane and dyad axis This system has also been styled the "monosymmetric," "clinorhombic," or the "oblique" system

EXAMPLES —Borax—$Na_2B_4O_7$ $10H_2O$, gypsum ferrous sulphate—$FeSO_4$ $7H_2O$, sodium carbonate—Na_2CO_3 $10H_2O$, felspar—orthoclase, sodium sulphate —Na_2SO_4 $10H_2O$, ammonium magnesium sulphate—K_2SO_4 $MgSO_4$ $6H_2O$ potassium chlorate, potassium tetrathionate—$K_2S_4O_6$, tartaric acid, sulphur—from fusion, cane sugar, arsenic disulphide—realgar, etc

III Rhombic system —Here the crystals may have three planes of symmetry, and three dyad axes of symmetry This system is sometimes called the "orthorhombic," "trimetric," or the "prismatic" system

EXAMPLES —Zinc sulphate—$ZnSO_4$ $7H_2O$, magnesium sulphate—$MgSO_4$ $7H_2O$, ammonium magnesium phosphate—NH_4MgPO_4 $6H_2O$, potassium sulphate arragonite, anhydrous sodium or silver sulphate sulphur from solution, barytes, sodium arsenate, sodium phosphate—NaH_2PO_4 H_2O, iodine; potassium nitrate, tartar emetic, potassium chlorate, potassium permanganate, topaz; marcasite, pyrrhotite, tin, tridymite, silver nitrate, lead carbonate, silver sulphide, ferrous sulphate—$FeSO_4$ $7H_2O$, etc

IV. Tetragonal system —The members of this system may have five planes of symmetry, one tetrad, and maybe four dyad axes of symmetry This system is sometimes called the "pyramidal," "quadratic," or the "quaternary" system

EXAMPLES —Rutile, cassiterite, zircon, mercurous chloride, potassium ferrocyanide, nickel sulphate, potassium hydrogen phosphate—KH_2PO_4, native lead molybdate—$PbMoO_4$, sodium meta *antimonite*—$NaSbO_3$, potassium hydrogen arsenate—KH_2AsO_4, scheelite, tin, strychnine sulphate, etc

V Trigonal system —The crystals of this system may have three planes of symmetry, one triad, and three dyad axes of symmetry. This system

is sometimes called the "rhombohedral" system, and it is sometimes regarded as a special development of the hexagonal system

EXAMPLES.—Sodium periodate—$NaIO_4.3H_2O$; quartz; tourmaline; antimony; bismuth; calcite; ice; graphite; sodium nitrate; arsenic; antimony; nickel sulphide—millerite; cinnabar; calcium chloride—$CaCl_2.6H_2O$; corundum; cadmium carbonate; bismuth iodide; ferrous carbonate; zinc carbonate; manganese carbonate; etc.

VI. **Hexagonal system.**—Here the crystals may have seven planes of symmetry, one hexad, and six dyad axes of symmetry.

EXAMPLES.—Beryl; apatite; cadmium sulphite—greenockite; copper sulphide; lead iodide; magnesium; beryllium; zinc; cadmium; calcium; pyrrhotite; etc.

VII. **Cubic system.**—The crystals in this system may have nine planes of symmetry, six dyad, three tetrad, and four triad axes of symmetry. This system has been variously styled the "isometric," "regular," "tesseral," "octahedral," or the "tessural" system.

EXAMPLES.—Diamond; potassium chloride; sodium chloride; alum; fluorspar; iron pyrites; lead nitrate; magnetic oxide of iron; barium nitrate; arsenic trioxide; galena; garnet; ammonium chloroplatinate; silver chloride; boracite; iron; platinum; lead; phosphorus; gold; copper; silver; arsenic; etc.

§ 5. The Internal Structure of Crystals

Imagine two hundred brilliant violin players playing the same piece with perfectly tuned instruments but commencing at different places selected at random. The effect would not be pleasing, and even the finest ear could not recognize what was being played. Such music is made for us by the molecules of gases, liquids and ordinary solids. They may be highly gifted molecules with a marvellous internal structure, but in their activity, each disturbs the others. A crystal, on the other hand, corresponds with the orchestra led by a vigorous conductor when all eyes intently follow his nod and all hands follow the exact beat. This picture enables us to understand how crystals can exhibit whole ranges of phenomena quite wanting in other bodies. To me, the music of physical law sounds forth in no other department in such full and rich accord as in crystal physics.—W. VOIGT.

Crystals are not only peculiar in the regularity of their external shape, but they also possess a definite internal structure. The properties of crystals are not always the same in different directions. The hardness, elasticity, crushing strength, rate of solution in acids, optical, thermal, and electrical properties are generally different in different directions. This means that the elasticity, refraction of light, thermal expansion, etc., of a crystal is usually different when measured in different directions.

In illustration, let a slice of quartz be cut perpendicular to the long axis, and another slice be cut perpendicular to this; let each slice be covered with wax, and pierced at the centre so that a wire can be inserted and heated by an electric current. The wax naturally melts about the hot wire. In the former case, the molten wax will form a circle; and in the latter case, an ellipse. If a crystal of calcite be hung in a beaker of dilute hydrochloric acid by means of a platinum wire, solution does not occur at a uniform rate over the whole surface, but the crystal dissolves more rapidly in one direction than in another. With salt, cubic system, the rate of solution is the same in all directions. Again, the rate at which light travels through cubic crystals is the same in all directions, but not with members of the other systems.

The external form of crystals is their most obtrusive characteristic, and it was naturally the first to arrest attention, but the geometrical shape is by no means the most characteristic property of crystals, because the external geometrical form may be destroyed, and yet the fragments do not cease to be crystals On the contrary, the most perfect glass model of a crystal is not a crystal, because it lacks the characteristic internal properties of crystals[1] In the case of granite (Fig 2), the crystals of felspar, quartz, and mica have been so crowded during their growth that they have had no chance to develop their characteristic external shape. The internal structure of each mineral, however, is characteristic A crystal has therefore been defined as "a solid body bounded by plane surfaces arranged according to definite laws, and possessed of definite physical properties Both the external form and the physical properties result from a definite internal structure" **The essential difference between crystalline and amorphous substances is one of internal structure, not necessarily external shape**

An amorphous substance is one which, during "solidification," has not taken the definite external shape characteristic of crystals, and the properties when measured in any one direction are the same as when measured in any other direction In this case it is assumed that the constituent molecules are arranged haphazard In crystals, on the contrary, where the properties along parallel directions are the same, but different in directions that are not parallel, it is assumed that the ultimate molecules, or their motions are oriented or arranged in a definite regular manner. W Voigt (1900) aptly illustrates this idea by the metaphor cited above

§ 6. The Growth of Crystals.

The very molecules appear inspired with a desire for union and growth — J TYNDALL

We do not understand the phenomenon of crystallization, nor do we know how crystals grow The facts indicated in the preceding sections have made us almost certain that crystals grow by accretion, molecule by molecule, like bricks in the hands of the builder, and in accord with "an architectural plan more elaborate and exact than that of any human architect" Whatever be the actual size and shape of the structural unit, it is equally certain that (1) *the structural units or molecules of crystals of the same chemical substance, under similar conditions, must be alike in size, and in the distribution of their attractive forces*, (2) *the relative position of any one molecule must be symmetrical with that of every other molecule*, and (3) *that the way the molecules are packed in and along all parallel planes must be the same* No other arrangement can be regarded as possible in a crystal Hence the study of crystal structure is reduced to the investigation of the possible arrangements of networks of structural units in space which satisfy these conditions Mathematicians have shown that 230 different methods of packing are possible, and that all these

[1] The shapes of gems cut and polished to accentuate the ornamental value of the gem must not be confounded with crystal structure Similarly, the term "crystal" applied to cut glass has a different meaning from the special use of the word "crystal" in the text Transparent glass is not crystalline, some varieties of opaque glass are more or less crystalline

can be classified into seven groups corresponding with the seven systems of crystal architecture indicated above

When a crystal is growing, curiously enough, the liquid in the immediate vicinity of the growing face is more concentrated, for it contains more of the dissolved substance per unit volume than the liquid a short distance away from the growing face. At first sight, it seems as if the growing crystal exerts some kind of attraction on the molecules of the dissolved substance a short distance away For instance, if a saturated solution of zinc silicate in molten lead borosilicate tinted with cobalt silicate be allowed to crystallize, the crystals of willemite which separate will also abstract the cobalt silicate from the solution, and form patches of beautiful "azure blue" crystals in a colourless matrix. If no crystallization occurs, the matrix will be uniformly coloured an intense blue

The kinetic theory of crystal growth—The kinetic theory has taught us that during crystallization it is probable that a series of exchanges between the molecules of the crystal and the molecules of the solution are going on all over the surface of the growing crystal Molecules of the dissolved substance are attracted to the surface of the growing crystal, the molecules of the crystal continually pass into solution again If the crystal is growing, more molecules are deposited on the crystal than are lost in unit time, and if the crystal is dissolving, less molecules are deposited on the crystal than are lost in a unit of time.

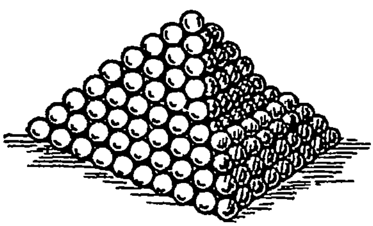


FIG 68—Imaginary Diagram of Growing Crystal

Let Fig 68 represent, diagrammatically, a growing crystal, one face of which is incomplete, and assume—as R Hooke did in 1665—that the structural units are spherical molecules. If a sphere lodges against a completed face, it can touch *three* other spheres, and whether or not the molecule leaves the growing crystal will depend upon the force of attraction exerted upon it by the three contiguous molecules Again suppose that a sphere lodges on the little ledge formed by the top layer of the incompleted face It will then touch *five* instead of *three* spheres, and it will be held in place by the attraction of five contiguous spheres

Obviously, therefore, (1) during the exchange of molecules between the growing crystal and the solution, those molecules which have been deposited on the growing face will be retained more tenaciously than those deposited on a completed face, (2) as soon as a few molecules happen to be deposited in juxtaposition on the face of a crystal, subsequent growth on that face will be more rapid than the sporadic growth elsewhere, (3) an incompleted layer will rapidly extend until it covers the entire face of the crystal, etc These deductions are in harmony with known facts In illustration, if one part of a crystal be damaged the injured part will grow more rapidly than the other parts of a crystal until the injury disappears, and the perfect crystal is restored Further, if a crystal be removed from a solution in which it is growing, it does not lose its power of growth, for if the crystal be placed in a suitable environment at any future time, it will continue growing as if there had been no interruption

These two statements are demonstrated by the sketch, Fig 69, from a remarkable photograph Some quartz crystals, grown during some former geological period, have lost their external crystalline form by attrition as they "knocked about the world"—blown about as sand in the deserts, washed down the hillside in streams of water, etc —and they were finally deposited as rounded sand grains along with the mountain limestone from some prehistoric sea There the damaged crystals—sand grains—met a suitable environment in later years—probably water percolating through the limestone rocks, and carrying silicic acid in solution The damaged crystals were repaired Each sand grain, now imbedded in each of the repaired crystals, served as a foundation for rebuilding the damaged quartz crystals on the original architectural plan

§ 7 Isomorphism—Mitscherlich's law.

While making preparations of the arsenates and phosphates of potassium and ammonium, E Mitscherlich, 1818, noticed that the crystals were so like each other as to be indistinguishable by simple inspection, and a closer examination led Mitscherlich to conclude (1) that bodies of different chemical composition may have the same crystalline form, (2) substances of similar constitution have the same crystalline form Mitscherlich wrote "*The same number of atoms combined in the same manner produce the same crystalline form, the crystalline form is independent of the chemical nature of the atoms, and is determined solely by their number and mode of combination*"—*Mitscherlich's law* He noticed that the acid arsenates and phosphates of potassium and ammonium crystallize in similar tetragonal forms, and that one element or group of elements may be exchanged for another which appears to act in an analogous manner Thus arsenic may be exchanged for phosphorus, and potassium for ammonium without affecting the form of the crystals. In Mitscherlich's words "Every arsenate has its corresponding phosphate, composed according to the same proportions, combined with the same amount of water of crystallization, and endowed with the same physical properties, in fact, the two series of salts differ in no respect except that the radicle of the acid in the one series is phosphorus, while in the other it is arsenic"

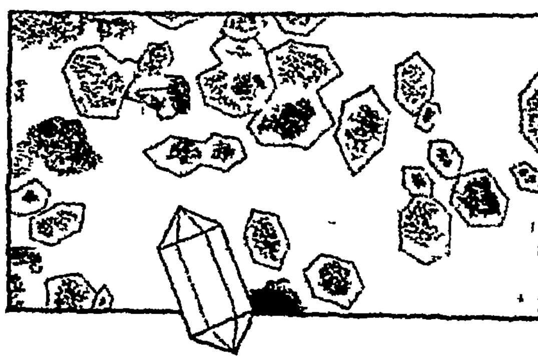


FIG 69 —Growth of Quartz Crystals about Sand Grains

Besides the phosphates and arsenates, Mitscherlich observed that mineral carbonates calcite—$CaCO_3$, dolomites—$CaMg(CO_3)_2$, chalybite—$FeCO_3$, and dialogite—$MnCO_3$—all form isomorphous crystals in the trigonal system (Fig 128), again, the mineral sulphates barytes—$BaSO_4$, celestine—$SrSO_4$, and anglesite—$PbSO_4$—all form similar rhombic crystals, aragonite, $CaCO_3$, witherite, $BaCO_3$, strontianite—$SrCO_3$, and

cerussite—$PbCO_3$, form isomorphous rhombic crystals (Fig 128), etc. Mitscherlich applied the term isomorphism—from the Greek ἴσος (isos), equal, μορφή (morphe), shape—to connote the fact that analogous elements can replace one another without affecting the apparent shape of the crystals

Mitscherlich s law of isomorphism, as well as the phenomena of polymorphism, appear to contradict Haüy's law (p 173), but later investigations have shown that the crystals of isomorphous substances are not absolutely identical, but only similar in form. There are small but real differences between the members of an isomorphous series of compounds. Thus, A. E H Tutton found that in the isomorphous selenates and sulphates of potassium, rubidium, and cæsium, specific chemical replacements are accompanied by clearly defined changes in the crystal structure along specific directions. Thus, when the basic element, say, potassium, in an alkaline, sulphate or selenate is replaced by another of the same alkali family group, rubidium or cæsium, the greatest alteration occurs in the crystal angles corresponding with an elongation of the vertical axis, and when the acid forming element sulphur is replaced by selenium its family analogue, the greatest expansion takes place along the horizontal axes of the crystals The diagram, Fig 70, shows, in an exaggerated manner, the effect of replacing potassium in potassium sulphate or selenate by the basic elements rubidium or cæsium.

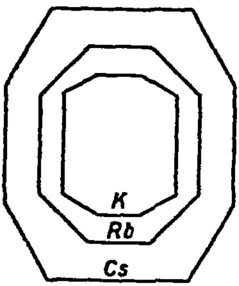


FIG 70
(After A. E H Tutton)

Retgers' law of mixed crystals —Extended observations have multiplied examples of substances which possess a similar chemical constitution and a similar crystalline form, but at the same time the observations have also brought into prominence the fact that substances which crystallize in similar or identical forms—particularly in the cubic system—may exhibit wide divergencies in chemical constitution The converse of Mitscherlich's law does not, therefore, hold good. Similarity of chemical composition or similarity in crystalline form are not adequate tests for isomorphism. Mitscherlich also stated that "while substances of different crystalline form cannot combine other than in fixed proportions, substances of the same crystalline form can crystallize together in all proportions", and J W Retgers (1889) considers all important the property of forming mixed crystals in all proportions such that "if the percentages of one constituent of the mixture be plotted as abscissæ, and the corresponding magnitudes of the physical properties be plotted as ordinates the different points lie in a continuous line," or the physical properties of isomorphous mixtures are continuous functions of the percentage composition—Retgers' law Physical properties here include geometrical, optical, thermal, elastic, and electrical properties, but on practical grounds, Retgers considers specific gravity, or the reciprocal of specific gravity—specific volume—to be the most suitable property for investigation. An example is indicated in Fig 71 where the specific volume of mixed crystals of potassium and ammonium sulphates are plotted The continuity of the curve shows that the specific gravity or specific volume and chemical composition of the mixed crystals are isomorphous. The curves sometimes show a break, as

is the case with Mitscherlich's phosphates, showing that the two substances are not miscible in all proportions, but the two portions of the curve are parts of one straight line corresponding with the isomorphous character of the two salts If the curve shows a kink or abrupt bend, the two salts even if perfectly miscible in all proportions, would not, according to Retgers' definition be called isomorphous For instance, ammonium and ferric chlorides are not isomorphous although octahedral ammonium chloride forms coloured mixed crystals by taking up a small amount of ferric chloride In special cases, double compounds may be formed which interfere with the application of Retgers' rule—e g potassium and silver nitrates form $KAg(NO_3)_2$, and potassium chloride and cupric chloride—$CuCl_2.2H_2O$—form $2KCl.CuCl_2.2H_2O$

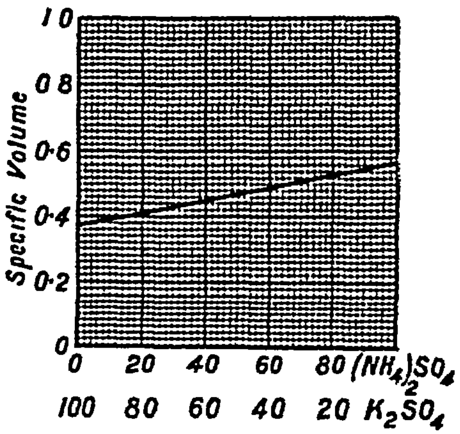


FIG 71 —Specific Volumes of Mixed Crystals of Ammonium and Potassium Sulphates

Overgrowths —If a crystal of dark violet chromium alum be placed in a saturated solution of ordinary potassium alum, a transparent colourless overgrowth of potassium alum is deposited as a crust over the dark-coloured chromium alum as a nucleus. Similarly, a crystal of colourless zinc sulphate—$ZnSO_4.7H_2O$—can be coated with an overgrowth of green nickel sulphate—$NiSO_4.7H_2O$; crystals of sodium nitrate grow on Iceland spar, and a pale amethyst triclinic crystal of manganese sulphate—$MnSO_4.5H_2O$—can be coated with blue copper sulphate—$CuSO_4.5H_2O$, etc H Kopp (1879) stated that this power of forming overgrowths, as well as the power of forming mixed crystals, enables isomorphism to be detected even when no particulars about the crystalline form or about the chemical composition are available There are some exceptions to the test for isomorphism—trigonal potassium sulphate can be coated with a layer of hexagonal potassium sodium sulphate—$KNaSO_4$

Tests for isomorphism —Substances which satisfy the three tests.

(1) Similarity of crystalline form (Mitscherlich),
(2) Formation of mixed crystals (Retgers), and
(3) Formation of overgrowths (Kopp),

are generally of analogous chemical constitution, and accordingly isomorphous None of these tests is an infallible criterion, and here, as is so often the case, a conclusion can be drawn only after carefully balancing the available circumstantial evidence

Isodimorphism —Each of the sulphates $RSO_4.7H_2O$ (where R may be Mg, Zn, Ni, Co, Fe, Mn) is dimorphous, forming rhombic and also monoclinic crystals The rhombic crystals of all the salts form one isomorphous series, and the monoclinic crystals of all the salts form another isomorphous series This phenomenon—two independent series of isomorphous salts—is called isodimorphism. Monoclinic felspar—orthoclase—often contains sodium, while triclinic soda felspar—albite—often contains

potassium Hence P Groth (1874) inferred that this is a case of isodimorphism, and that two pure varieties—monoclinic and triclinic soda and potash felspars should exist The prediction was verified two years later by the discovery of microcline, the triclinic form of potash felspar, and later still by the discovery of barbierite, the monoclinic form of soda felspar Sodium phosphate forms two distinct crystals—rhombic and monoclinic The arsenate appears in only one of these forms Hence it is inferred that a monoclinic sodium arsenate isomorphous with rhombic sodium phosphate remains to be discovered

§ 8 The Rectification of Atomic Weights by Isomorphism

The law of isomorphism can be used as a control in deducing the chemical composition of a salt, and also in atomic weight determinations for deciding between two numbers which are multiples of a common factor The method is restricted to crystalline compounds, and it is only applicable in conjunction with other methods of atomic weight determinations since at least one member of the isomorphous series must be known.

Mitscherlich deduced the number 79 for the atomic weight of selenium by this method, and he also gave selenious and selenic acids formulæ corresponding with sulphurous and sulphuric acids respectively, on account of the isomorphism of the sulphates and the selenates The analyses of potassium sulphate and of potassium selenate gave

	Potassium.	Oxygen.	Sulphur	Selenium	Total
Potassium sulphate	44 83	36 78	18 39	—	—100 00
Potassium selenate	44 83	36 78	—	45 40	—127 01

Assuming that the molecule of potassium sulphate contains one atom of sulphur, that the molecule of potassium selenate contains the same number of atoms, and that the atomic weight of sulphur is 32, we have

$$\text{Atomic weight S} \quad \text{Atomic weight Se} = 18\ 39 \quad 45\ 34$$

Hence,

$$32 \quad \text{Atomic weight Se} = 18\ 39 \quad 45\ 34$$
$$\text{Atomic weight of selenium} = 79\ 00$$

About 1836 the atomic weight of copper was supposed to be 63 4, and of silver, 216 6 The analysis of the native sulphides of these elements were accordingly represented by the formulæ Cu_2S and AgS But J B Dumas (1837) pointed out that the two minerals are isomorphous, and various mixed sulphides of the two elements are known by the general term "fahlore." Hence the constitution of the two sulphides is probably the same. Assuming the formula of the one is Cu_2S, the formula of the other will probably be Ag_2S, and the atomic weight of silver 108 3, not 216 6 This result agrees with evidence deduced from other independent sources. More exact determinations of the atomic weight of silver make this element 107·9, but this does not affect the principle of the argument

EXAMPLE.—Analyses of alumina show that Al O = 18 1 16, the equivalent of aluminium is 9 03, hence the formula of alumina might be

	AlO	Al_2O_3	AlO_2	AlO_3
O Al	16 18 1	48 27 1	32 36·2	48 54 2

that is the atomic weight of aluminium might be 18 1 27 1, 36 2, 54 2 There is nothing in the composition of the oxide to show which of these numbers should be selected It is known, however, that ferric oxide—Fe_2O_3—forms a series of iron alums isomorphous with the aluminium alums hence it is inferred that the constitution of aluminium oxide is Al_2O_3 and that the atomic weight of aluminium is 27 1

Questions

1 State the law of isomorphism and give examples of its utility in fixing the atomic weights of elements —*St Andrews Univ*

2 "Sodium sulphite, $Na_2SO_3 \cdot 7H_2O$, forms colourless *monoclinic crystals*, with a *saline taste*, and *alkaline reaction* The crystals *effloresce* in dry air, they are *soluble* in water, and become *anhydrous* when heated to 150° At a higher temperature the crystals *decompose* forming a yellow liquid" Explain the meaning of the terms in italics in this quotation

3 "The *element* sulphur is *dimorphous* It occurs in both *rhombic and monoclinic crystals*, and also in an *amorphous* condition" Explain the meaning of the terms in italics in this quotation

4 Discuss the statement of Mitscherlich that equal numbers of atoms similarly combined exhibit the same crystalline form, identity of crystalline form being independent of the chemical nature of the atoms, but conditioned only by their number and configuration Point out the precise value, as well as the limitations of this "law" as regards its bearing on chemical classification —*Science and Art Dept*

5 State the law of isomorphism, illustrate its application to the determination of the class relations of the elements, and point out apparent exceptions to the law —*London Univ*

6 Explain the meaning of the terms solution, saturated solution, and crystallization Show how it can be proved experimentally that hot water is generally a better solvent than cold water —*Cape Univ*

7 If the solubility of sodium chloride in water at 20° is 35 6, how much water will be needed at this temperature for the solution of a kilogram of the salt ?

CHAPTER XI

Ozone and Hydrogen Peroxide

§ 1 The Modes of Formation, and Preparation of Ozone

Ozone Molecular weight $O_3 = 48$ Boiling point about $-120°$ Relative vapour density ($H_2 = 2$), 46 65, (air = 1) 1 62

The Formation of Ozone—Ozone is produced by the action of the ultra violet rays and radium radiations on oxygen Ozone can generally be detected in the oxygen gas obtained during the electrolysis of acidulated water (p 20) By the electrolysis of sulphuric acid (between 1 075 and 1 1 specific gravity), with an anode made by imbedding platinum foil in glass and grinding away the edge so that a line of platinum, 0 1 mm broad, is exposed, oxygen containing 17 to 23 per cent of ozone has been obtained The presence of ozone can be shown by means of a strip of paper wetted with a solution of starch and a little potassium iodide The paper so prepared becomes blue with ozone, not with oxygen

The oxygen liberated by many reactions also contains ozone For instance, manganese dioxide and sulphuric acid, barium dioxide and sulphuric acid, potassium permanganate and sulphuric acid, persulphuric acid, etc When fluorine decomposes water forming hydrogen fluoride and oxygen, from 13 to 14 per cent of the "oxygen gas" is ozone

Ozone is formed during the slow oxidation of many substances Ozone can be detected in the atmosphere of a flask containing a couple of sticks of clean phosphorus. Ozone is said to be formed during the combustion of ether as well as during the combustion of hydrogen compounds generally At any rate, the potassium iodide test indicates the formation of ozone (or hydrogen peroxide) when a spiral of hot platinum is placed above the surface of a little ether in the bottom of a beaker The ether burns on the surface of the platinum, and the platinum remains incandescent as long as any ether remains in the beaker Again if a strong jet of air be blown through the upper portion of a Bunsen's flame, or if a very narrow tube be presented to the lower edge of a Bunsen's flame and a slow current of air be aspirated through a little potassium iodide dissolved in water, the ozone (or hydrogen peroxide) reaction is obtained

Ozone seems to be fairly stable at ordinary temperatures although it gradually decomposes on standing It also appears to be fairly stable at high temperatures, while at intermediate temperatures it is unstable Hence ozone may be formed by heating oxygen to a high temperature, and, by suddenly chilling the gas, it can be cooled below the temperature at which it is very unstable without being all decomposed The chilling can be done by blowing air or oxygen against the hot pencil of a Nernst's burner, or by dipping a hot Nernst's pencil, or hot platinum wire in liquid air

Method of preparing ozone —The most usual method of making ozone, or rather of preparing ozonized air and ozonized oxygen is to expose air or oxygen to a silent discharge of electricity Quite a number of instruments are available That illustrated at *AB*, Fig 72, is virtually the one devised by W von Siemens (1858) It consists of two concentric tubes The inner tube is coated on its inner surface with tinfoil in metallic contact with the terminal *A*, and the outer tube is coated on its outer surface with tinfoil in metallic contact with the terminal *B* The two terminals are connected with an induction coil A slow stream of oxygen is led from the gasholder *C* through the calcium chloride drying tube *D*, and then through the annular space between the concentric tubes, and is there exposed to the action of the silent discharge of electricity, operated

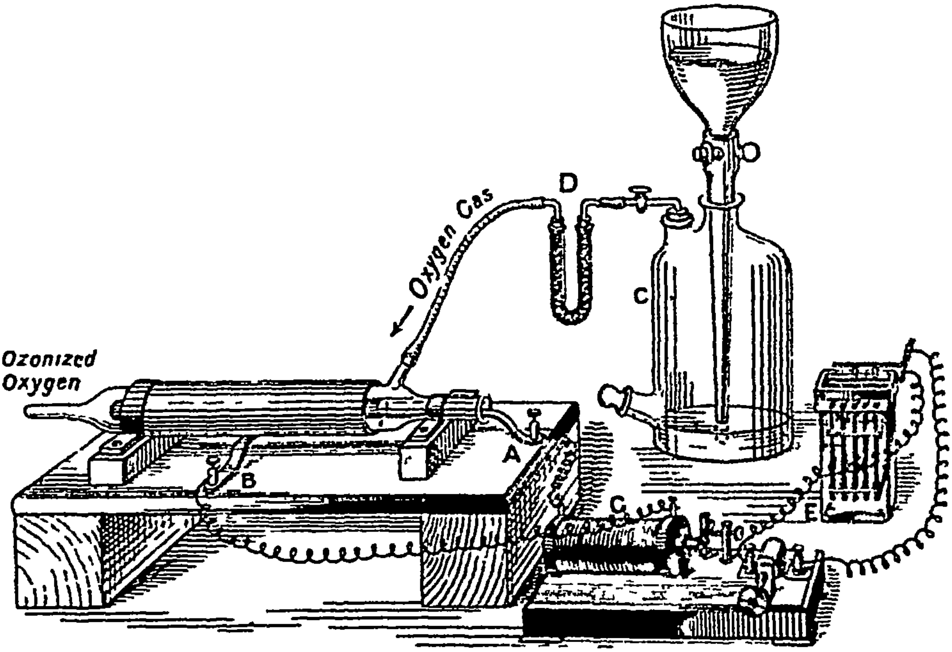


Fig 72 —Preparation of Ozone with Siemens' Tube

by the induction coil, *G*, and battery *E* The gas issuing from the ozone tube or ozonizer is charged with 3 to 8 per cent. of ozone In Berthelot's ozone tube the tinfoil coatings are replaced with sulphuric acid (Fig 76) If air be used in place of oxygen, some nitrogen oxides are said to be formed at the same time The presence of moisture is said to reduce the yield of ozone,[1] although no difference has been detected in the amount of decomposition of the dry and moist gas when heated for some time at 100°.

§ 2 The Properties and Occurrence of Ozone

Ozonized air has a strong unpleasant smell The smell reminds some people of sulphur dioxide, others of garlic, and others of chlorine *If air* highly charged with ozone be breathed for any length of time, it produces

[1] Ozone is decomposed by cork and indiarubber In consequence, these materials should not be used for any part of the ozonizer in contact with the gas

headache, but in minute quantities the odour is pleasing and refreshing. Ozone is soluble in water—100 volumes of water at ordinary temperatures and pressure dissolve about one volume of ozone—and the water smells of the ozone and exhibits many of the properties of ozone. The water slowly reacts with the ozone.[1] Ozone is dissolved by essential oils—turpentine, thyme oil, cinnamon oil, etc.

Action on potassium iodide.—Unlike oxygen, ozone liberates iodine from neutral potassium iodide. This can be shown by dipping paper in a solution of potassium iodide and holding it at the exit tube of the ozonizer. The paper turns brown owing to the liberation of iodine. If a little starch be mixed with the potassium iodide, the paper will appear blue. The reaction is usually represented:

$$\underbrace{O_3}_{\text{Ozone}} + 2KI + H_2O = \underbrace{O_2}_{\text{Oxygen}} + I_2 + \underbrace{2KOH}_{\text{Potassium hydroxide}}$$

The potassium hydroxide is alkaline. Hence if red litmus paper be steeped in water containing a trace of potassium iodide, the moist paper, when exposed to ozonized air, will be coloured blue owing to the action of the potassium hydroxide on the red litmus. If ozone acts upon an acidified solution of potassium iodide, the result is different from that which occurs with neutral potassium iodide. The action also depends upon the temperature and the strength of the solution (B. Brodie, 1872).

The method used for the determination of ozone in air, etc., is based upon the reaction symbolized above. A known volume of air is drawn through a neutral solution of potassium iodide, and the liberated iodine is determined by acidifying the solution, and titrating the liberated iodine with a standard solution of sodium thiosulphate, as will be indicated later. The standard method for estimating ozone in, say, the atmosphere is to expose ozone test papers[2] for a definite time to the air and compare the resulting tint with a standard scale of colours obtained with air containing known quantities of ozone. Since other oxidizing substances, likely to be present in air, produce a similar reaction, it is a moot question whether the large number of "ozone determinations" which have been made really represent ozone, or hydrogen peroxide, nitrogen oxides, chlorine, etc. Rather does the result of the test represent the presence of "oxidizing substances."

Oxidizing action of ozone.—Ozone is a very powerful oxidizing agent. Paper coloured by a solution of indigo sulphate or a solution of litmus is bleached. Other substances—hydrogen peroxide, chlorine, nitrogen oxide, etc.—give these reactions and hence the tests do not distinguish between ozone and the compounds just named. Put a globule of mercury in a small flask, pass ozonized air into the flask and shake the globule of mercury about. The mercury loses its lustre, and spreads a film over the walls of the flask. The globule mercury is restored when the film is shaken up with water. If a piece of silver foil cleaned with silver sand be heated in a Bunsen's burner for a moment and while still warm, held in a stream of ozonized air, the silver is blackened, owing, it is said,

[1] The so called "ozone water" is largely a mixture of nitrogen oxide, chlorine, hypochlorous acid, and calcium hypochlorite.

[2] Papers steeped in an emulsion of starch containing a small proportion of potassium iodide are called ozone test papers.

to the formation of silver peroxide Silver perfectly free from the oxide does not show the reaction—H Thiele (1906) A trace of oxide is supposed to be formed when the silver is heated in the Bunsen's burner. The reaction is characteristic of ozone, but *it is not very sensitive* Ozone converts dark brown coloured lead sulphide into white coloured lead sulphate $PbS + 4O_3 = PbSO_4 + 4O_2$ This can be shown by holding a strip of paper, which has been steeped in a solution of lead acetate and "browned" by hydrogen sulphide, in a stream of ozonized oxygen or ozonized air Many other sulphides—copper, antimony, zinc, cadmium—behave in a similar manner Nickel and cobalt sulphides form peroxides and sulphuric acid.

The action of ozone on peroxides—Ozone decomposes in the presence of finely divided platinum, lead dioxide, manganese dioxide, silver and copper oxides. The ozone is converted into ordinary oxygen without decomposing the oxides Hence the reactions are grouped among catalytic reactions The effect can be shown by passing ozonized air through a tube containing copper oxide and testing the issuing gas by ozone test paper No indication of ozone is obtained When ozone is brought into contact with sodium peroxide, the two substances mutually decompose and oxygen is liberated $O_3 + Na_2O_2 + H_2O = 2NaOH + 2O_2$

The action of the silent discharge on ozone—The silent discharge has a de ozonizing as well as an ozonizing effect on oxygen The speed of the ozonization is proportional to the amount of oxygen present, and the speed of the deozonization is proportional to the amount of ozone present In other words, the reaction follows the law of opposing reactions If the discharge be passed an infinite time, a certain definite limiting concentration of ozone will be reached when the rate of decomposition is equal to the rate of formation of the ozone $3O_2 \rightleftharpoons 2O_3$ The greater the pressure of the gas, the greater the yield, and if the density of the gas be kept constant, the yield of ozone is not very different at temperatures between 10° and 80° The presence of moisture also reduces the yield (E Warburg, 1906)

The action of heat on ozone—Ozone decomposes slowly at ordinary temperatures, and the rate of decomposition is increased by raising the temperature According to E Warburg (1902), at 16°, one per cent of pure ozone per litre of oxygen decomposes in 1 7 minutes, at 100°, in 0 003 minute, at 127°, in 0 0027 minute, and at 1000° the decomposition is almost instantaneous, for 0 0007 second suffice for the decomposition of $\frac{999}{1000}$ of the ozone present Hence to show the formation of ozone at high temperatures, the velocity of cooling must be greater than the rate of decomposition If a tube be attached to the exit tube of the ozonizer so that a slow current of ozonized oxygen can be passed through the tube heated to about 300°, the issuing gas will give no reaction for ozone with the ozone test papers Since ozone is formed at very high temperatures, there must be a reversal in the *stability*, before the temperature of formation is reached.

The effect of cooling ozone—By passing ozonized oxygen through a tube cooled by immersion in boiling liquid oxygen, or by ozonizing oxygen in a tube kept at this temperature, a solution of ozone in liquid oxygen is obtained By allowing the liquid to boil most of the oxygen is removed In this manner a deep indigo blue liquid is obtained which is

opaque in layers 2 mm thick The liquid is said to be explosive By allowing the blue liquid to vaporize A Ladenburg (1898) obtained a gas containing about 86 per cent. of ozone

The effusion of gases—T Graham (1832) found that the law of diffusion, indicated on p 105, holds good for the passage of a gas through a very fine aperture in a metal plate Graham called the phenomenon the effusion of gases. The speed of effusion is therefore inversely as the square root of the specific gravity If a gas of density D_1 flows out of the tube in the time t_1 and another gas of density D_2 flows out in the time t_2 then, according to the law of effusion $D_1 : D_2 = t_1^2 : t_2^2$ R Bunsen (1857) utilized this fact to determine the specific gravity of a gas when but a small quantity of the gas is available. In N H. Schilling's effusion apparatus (1879) the gas is introduced into a glass tube, luted to a brass cover, via the cocks B, C, Fig 73 This tube is placed in a cylinder filled with water and the temperature is indicated by the thermometer T The perforated platinum plate is fixed at B The time taken for the water to press the gas from the level O to the level P on the cylinder is noted The experiment is repeated with another gas of known density A Ladenberg (1898) used this apparatus to determine the specific gravity of ozone

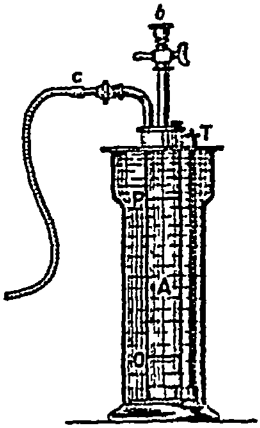


Fig 73—Schilling's Effusion Apparatus

EXAMPLE —A Ladenberg (1898) found that a mixture containing 86·16 per cent of ozone required 367·5 seconds to effuse under conditions where pure oxygen required 430 seconds Hence determine the specific gravity of ozone From the example on p 105 it follows that the specific gravity of the ozonized oxygen is 1·3698, oxygen = 1 From the example on p 19 it follows that the specific gravity of ozone is 1·456 if oxygen be unity and 46·6 if oxygen O_2 be 32 Note that this does not establish the molecular weight by Avogadro's hypothesis because in determining the proportion of ozone in the mixture, by estimating the amount of iodine liberated by a given volume of the gas, it was assumed that the reaction proceeds as indicated in a preceding equation which in turn assumes that the formula of ozone is O_3

Occurrence of ozone—Some samples of fluorspar are said to contain traces of ozone Ozone is supposed to occur in small quantities in the atmosphere near the seaside where it is supposed to be formed by the evaporation of water According to A. Houzeau, country air contains about one volume of ozone per 700,000 volumes of air The maximum amount of ozone in the atmosphere is said to occur during the spring months, and gradually diminishes, reaching a minimum in winter Ozone is absent in the air of towns, dwelling houses, over marshes, and wherever organic matter is present It has been shown that much of the alleged ozone may not be ozone at all This is due to the imperfection of the tests employed (p 186) T Andrews found that "oxidizing matter" in the air was destroyed by heating the air to 260° This would not be the case if the oxidizing matter was chlorine or nitrogen oxide But we shall see very shortly that Andrews' test does not discriminate between ozone and hydrogen peroxide Hence there is some uncertainty about many of

the reactions where ozone is supposed to be formed, and also in many reports of the proportion of ozone in the atmosphere.

The distinction between ozone and hydrogen peroxide.—C. Arnold and C. Mentzel (1902) propose the use of test papers soaked in an alcoholic solution of "tetramethyl base." These are not affected by hydrogen peroxide, but are turned violet with ozone, blue, with chlorine and bromine; and straw yellow, with nitric oxide. C. Engler and W. Wild (1896) state that if a mixture of ozone and hydrogen peroxide be passed through a concentrated solution of chromic acid, the hydrogen peroxide is alone decomposed, the ozone is not affected. The same investigators say that paper steeped in a concentrated aqueous solution of manganous chloride is turned brown by ozone, but not by hydrogen peroxide.

Uses.—Ozone is used for the purification of water. Its function is to oxidize the organic matter, and sterilize the water. Ozonized air is also used in ventilation, for bleaching oxidizing oil in the manufacture of linoleum, etc. The industrial applications have stimulated inventors, and accordingly a number of fairly efficient ozonizers have been placed on the market. In most of these, a *high tension alternating electric discharge* is sent across a space through which the air to be ozonized passes.

§ 3 The History and Constitution of Ozone.

1. The discovery of ozone by Schönbein (1840).—In 1775 M. van Marum said that he noticed a peculiar smell in the vicinity of electrical machines in motion, but he does not appear to have made any attempt to find the cause of the smell. C. F. Schönbein (1839–80) was the first to recognize that the smell was due to the formation of a substance to which he gave the name ozone—from the Greek ὄζω (ozo), I smell. According to Schönbein, ozone is a distinct form of matter with an identity of its own. Schönbein found that the same substance was produced when an electrical machine is working; when water is electrolyzed; and when moist air is passed over oxidizing phosphorus. The nature of ozone was the subject of much discussion in Schönbein's day. Schönbein first considered it to be a new elementary body which was a component of the nitrogen in the atmosphere.

2. Is ozone a condensed form of oxygen or an oxide of hydrogen?—C. Marignac, A. de la Rive, and others (about 1845) showed that moist silver, when exposed to ozone, forms silver oxide, and that potassium iodide—KI—can be oxidized to potassium iodate—KIO_3. This narrowed the question, for it appeared that ozone is either (1) a form of matter identical with oxygen (C. Marignac, A. de la Rive); or (2) oxidized water, that is, a peroxide of hydrogen (Schönbein). The hydrogen oxide theory was not given up until 1860, when T. Andrews and P. G. Tait proved that if an electric discharge—silent or spark—be passed through pure dry oxygen a contraction occurs amounting to $\frac{1}{12}$ of the original volume. The oxygen was sealed in a tube, shaped as indicated in Fig. 74, *Q*, and subjected to the silent discharge, *viâ* the platinum wires sealed into the glass. In Andrews and Tait's experiment, the contraction in volume was measured by attaching to the tubes a small manometer, *a* and *b*, charged with concentrated sulphuric acid. A duplicate tube *Q*, Fig. 75, containing air was treated along with the tube containing the oxygen, *R*, Fig. 74, so that

any changes due to variations of pressure or temperature during the experiment could be corrected The tubes during the experiment, were placed in a water tank, as indicated in Fig 75, to keep the temperature uniform When ozonized oxygen is heated to 270°, and allowed to cool, the original volume of oxygen is obtained and when a thin glass bulb, *c*, Fig 74, *R*, of potassium iodide is sealed in the tube along with the oxygen, and after ozonization, broken by shaking the bulb against a piece of glass tubing *d*, iodine is liberated without any perceptible change in volume If the gas which has been treated with potassium iodide be heated to 270° as before, no change in volume can be detected Hence Andrews and Tait concluded that ozone is a condensed form of oxygen This, however, tells us nothing about the weight of oxygen in a given volume of ozone, *i e.* the number of atoms in the molecule of ozone

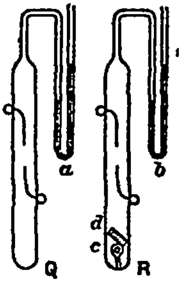


FIG 74 —Andrews and Tait's Ozone Tubes

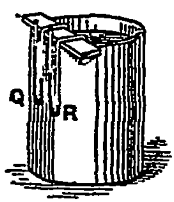
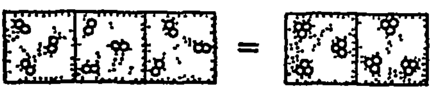


FIG 75 —Andrews and Tait's Experiment

The absence of hydrogen in ozone was inferred by Soret (1863) from an experiment in which ozone was thoroughly dried, and then decomposed by heat. No trace of any compound of hydrogen—*e g* water—could be detected in the products of decomposition Hence it is inferred that ozone is not a compound of hydrogen with oxygen , ozone contains nothing but oxygen A similar experiment was made by Schönbein in 1849, but its importance does not appear to have been appreciated.

3 Ozone is a form of oxygen in which three volumes of oxygen are condensed to two volumes —Since the volume of ozonized oxygen undergoes no change when mixed with a solution of potassium iodide, it is inferred that the oxidation of potassium iodide can only be effected by so much oxygen in ozone as has been condensed with ordinary oxygen to form ozone This excess of oxygen is absorbed by the solution of potassium iodide, and the ordinary oxygen which remains has the same volume as the ozone present before the action of the potassium iodide Hence no new contraction occurs with potassium iodide In symbols, the formula for ozone is O_{2+n} Andrews and Tait did not determine the numerical value of n The formula for ozone might be O_3, O_4, O_5 The special difficulty involved in this determination arises from the fact that ozone cannot be obtained free from oxygen , and, accordingly, the regular methods of determining the molecular weights—vapour density, etc —cannot be applied. W Odling (1861) proposed to take the simplest possible formula O_3, thus assuming that three volumes of oxygen are condensed to form two volumes of ozone Interpreting this unproved assumption in the light of Avogadro's hypothesis, p 57, we have



3 Volumes oxygen give 2 Volumes ozone.

Soret (1866) took advantage of the fact, known to Schönbein, that essential oils absorb ozone without decomposition Hence, if ozonized oxygen be shaken with, say, cinnamon oil, the ozone will be removed from the mixture On treating one portion of a sample of ozonized oxygen with cinnamon oil, Soret found that a contraction corresponding with about 2 c c was obtained. On heating another portion of the same sample so as to convert the ozone into ordinary oxygen, Soret found an expansion corresponding with 1 c c Hence it was inferred that three volumes of oxygen produce two volumes of ozone Soret's work was rather crude, but B Brodie (1872) repeated the experiments with cinnamon oil, turpentine, stannous chloride, in such a way that the above conclusion was the only possible interpretation of the experiments

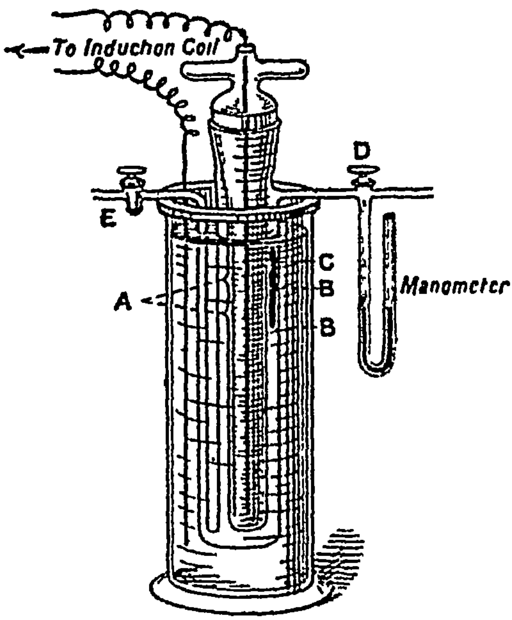
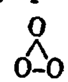


FIG 76—Newth's Apparatus (modified).

Many neat ways of illustrating the volume relations of oxygen and ozone have been devised G S Newth's apparatus (1896), slightly modified, consists of two concentric tubes, Fig 76. The inner tube has a hollow stopper ground to fit the outer tube It contains dilute sulphuric acid The inner tube has two little projections *A*, and the outer tube has three projections, *B*, in such a position that a sealed thin glass tube containing cinnamon oil can be broken, when desired, by twisting the stopper or the inner tube The outer tube is fitted with three way cock *D*, connected with a manometer charged with concentrated sulphuric acid The apparatus is placed in a cylinder containing, say, ice and water The annular space between the two tubes is filled with oxygen, *via* the cocks *E* and *D* The manometer is then put in communication with the annular space between the two tubes Note the level of liquid in the manometer Pass a current from an induction coil, so as to ozonize the oxygen sufficiently to give, say, a one centimetre contraction on the manometer Note the contraction Give the stopper a twist so as to break the glass tube containing the cinnamon oil, the contraction which occurs will be twice the former contraction, namely 2 cm more[1] The same apparatus can be employed for showing that no contraction occurs when ozone is treated with potassium iodide by using a tube *C* with this substance in place of cinnamon oil

The formula for ozone—O_3—obtained by many modifications of this experiment has been confirmed by the application of Graham's diffusion test, p 188 Ozone is 1 5 times as heavy as an equal volume of oxygen

4 **The graphic formula for ozone.**—Ozone is generally symbolized graphically



But owing to the peculiar oxidizing qualities of the odd oxygen atom in the molecule some consider that the three oxygen atoms are not symmetrically placed in the molecule, whereas in the above

[1] It may be advisable to level to the liquid in the manometer, after the first contraction, before breaking the capillary tube, by admitting either air or oxygen.

formula they apparently all have equal value. Ozone is often considered to be a compound of one quadrivalent oxygen atom with two bivalent oxygen atoms, and the formula is accordingly written $O{=}O{=}O$, or, if two quadrivalent oxygen atoms are united with one bivalent oxygen atom $\overset{\displaystyle O}{\underset{O\equiv O}{\wedge}}$, hence, the graphic formula for ozone is still *sub judice*

Belief in the existence of quadrivalent oxygen atoms is mainly based on evidence deduced from organic chemistry For instance, hydrogen chloride sulphur dioxide methyl iodide, etc, can be made to combine directly with methyl ether $(CH_3)_2O$ to form a series of compounds

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!O \qquad \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!O\!<\!\begin{matrix}H\\Cl\end{matrix} \qquad \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!O{=}SO_2 \qquad \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!O\!<\!\begin{matrix}CH_3\\I\end{matrix}$$

and also a series of oxonium salts These compounds are not discussed in inorganic chemistry Evidence in favour of a sexivalent oxygen atom has been brought forward, the so-called ozonic acid H_2O_4, of A. Bach (1902), and other organic compounds might be cited in illustration Hence oxygen, though usually bivalent, may be quadrivalent and probably also sexivalent

§ 4 Hydrogen Peroxide or Hydrogen Dioxide—Formation and Preparation

Molecular weight, $H_2O_2 = 34{\cdot}02$ Melting point $-2°$ boiling point, 84°–85° at 68 mm pressure, and at 26 mm pressure, 68°–69° Specific gravity, 1·4996

Hydrogen peroxide is formed when oxygen is bubbled about the electrode from which hydrogen is being evolved during the electrolysis of dilute acid, p 20 Water confined in a quartz vessel is decomposed by exposure to ultraviolet light rays—from a mercury lamp sunlight, etc—and hydrogen peroxide and hydrogen are formed $2H_2O = H_2O_2 + H_2$. Hydrogen peroxide is produced during the combustion of hydrogen in air For instance, when a jet of burning hydrogen impinges on the surface of cold water in which ice is floating, or on ice itself, hydrogen peroxide can be detected in the water Hydrogen peroxide is formed when moist ether is exposed to sunlight, and when ozonized oxygen or air is passed through water on the surface of which a little ether floats. If a little water is placed in a beaker containing ether, and the latter is burnt by placing a spiral of hot platinum wire just over the surface of the liquid (p 184), hydrogen peroxide can be detected in the water after all the ether has burnt away It is supposed that the ozone first produced forms a peroxide with the ether and that this is decomposed by the water reforming ether and hydrogen peroxide.[1]

Like ozone, hydrogen peroxide can be formed at a high temperature by passing a current of moist oxygen through a tube at about 2000° and rapidly chilling the issuing gases In H St. C Deville's "hot and cold tube" method of conducting the experiment, a narrow silver or platinum tube is kept cool by a current of cold water This tube is placed in the centre of a porcelain tube, Fig 77 A current of gas is passed along the annular space between the two tubes This arrangement is placed in a furnace so that the gas can be heated to a very high temperature. The products of decomposition are suddenly chilled by the

[1] The ether is thus regarded as a catalytic agent, and the reaction is supposed to proceed by a set of consecutive reactions, p 135

cold tube and partially prevented from recombining as they are carried out of the hot zone. The products of many high temperature reactions can thus be examined at ordinary temperatures.

Hydrogen peroxide is often formed when a substance is oxidized in the presence of moisture. For instance when zinc copper, or lead is shaken up with air and dilute sulphuric acid (1:55), the reaction symbolized: $Zn + 2H_2O + O_2 = Zn(OH)_2 + H_2O_2$; and $Zn(OH)_2 + H_2SO_4 = ZnSO_4 + 2H_2O$ occurs. It will be observed that twice as much oxygen is required for the oxidation process as is actually consumed in oxidizing the zinc. $Zn + O_2 = ZnO + O$; $H_2O + O = H_2O_2$. One half of the oxygen is said to be used in the primary process and the other half in the secondary reactions. The reaction belongs to the type of concurrent or side reactions discussed on p. 137, but since half a molecule of oxygen is used in each, the two concurrent reactions are not independent of one another. This particular type of reaction is known as auto-oxidation. There is a considerable difference of opinion as to the mechanism of auto-oxidation. The oxygen used in the secondary reaction—formation of hydrogen peroxide—is said to be 'rendered active' by the primary reaction The formation of ozone during the oxidation of phosphorus (p 184) is another example

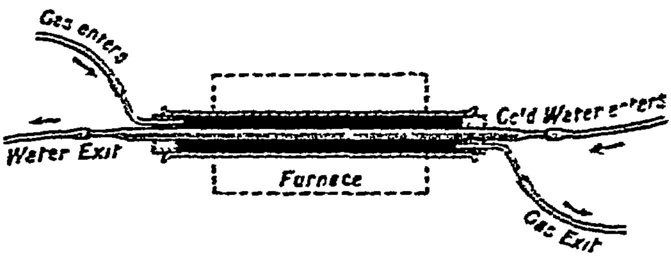


FIG 77—Deville's 'Hot and Cold Tube."

By treating a cold aqueous solution of sodium peroxide with dilute and cold hydrochloric acid, a solution of hydrogen peroxide in sodium chloride is obtained $Na_2O_2 + 2HCl = 2NaCl + H_2O_2$, and by treating potassium peroxide with tartaric acid in the cold, an aqueous solution of hydrogen peroxide contaminated with a little potassium tartrate is obtained. Most of the potassium tartrate separates from the cold solution

Barium peroxide (p 132) is the usual starting point for the preparation of hydrogen peroxide Gradually add barium peroxide to ice-cold water through which a stream of carbon dioxide is passing The insoluble barium carbonate is precipitated, and a dilute aqueous solution of hydrogen peroxide remains: $BaO_2 + CO_2 + H_2O = BaCO_3 + H_2O_2$. If an excess of carbon dioxide be used, the yield of hydrogen peroxide is low and an insoluble barium percarbonate, $BaCO_4$ is precipitated Or barium peroxide, mixed with a little ice cold water is gradually added to ice-cold dilute hydrochloric, sulphuric, silico-fluoric, or phosphoric acid A barium salt—chloride, sulphate, silicofluoride or phosphate—and hydrogen peroxide are formed. In the first case, the barium chloride is soluble. It can be removed by adding just sufficient silver sulphate to precipitate insoluble barium sulphate and silver chloride $BaCl_2 + Ag_2SO_4 = BaSO_4 + 2AgCl$. This method is of historical interest because J. Thenard employed a similar process when he discovered hydrogen peroxide in 1818 The sulphuric acid process is more commonly used. In this, insoluble barium sulphate is precipitated.

The preparation of almost pure hydrogen peroxide.—Barium peroxide, suspended in a little water, is gradually added to a mixture of equal volumes of water and sulphuric acid (cooled by a freezing mixture of ice and salt) until the solution is just barely acid. If too much barium peroxide has been added, a little more sulphuric acid is needed. Keep the solution in a freezing mixture for about a day. Filter off the insoluble matter, and evaporate the liquid on a water-bath, at about 70°, in a smooth platinum or porcelain basin until signs of effervescence appear. This will occur when the solution contains about 45 per cent. of hydrogen peroxide. Cool the solution quickly. Concentrated solutions soon decompose if they are not kept cold.

A solution of hydrogen peroxide decomposes rapidly when heated to 100°—even if the solution be dilute. R. Wolffenstein (1902) discovered that the hydrogen peroxide can be distilled under reduced pressure without undue decomposition, p. 158.

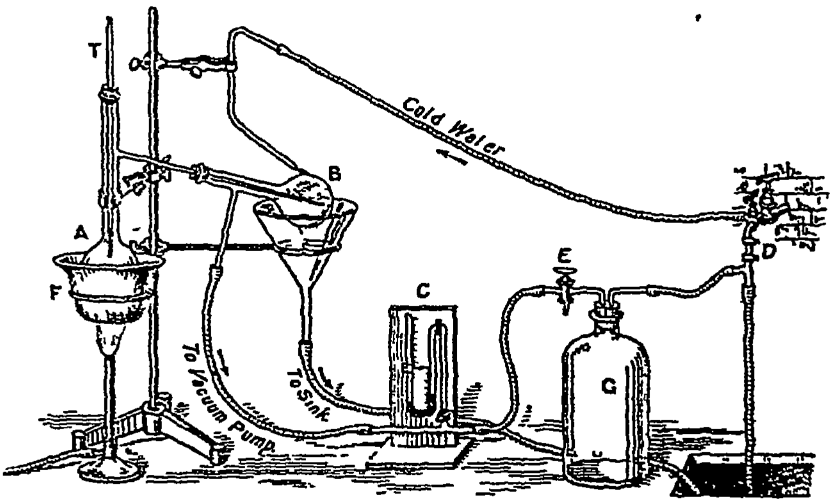


FIG. 78.—Distillation of Hydrogen Peroxide under Reduced Pressure.

To distil the solution under reduced pressure, fit up the apparatus indicated in Fig. 78. Transfer the solution to a round bottomed thick walled litre flask *A*, fitted with a receiver *B* and a thermometer *T*, by means of one-hole rubber stoppers. The receiver *B* is placed over a funnel so that cold water can be sprayed on the receiver, and run off to the sink through rubber tubing attached to the stem of the funnel. The side neck of the receiver is connected, by pressure tubing, with a manometer, which in turn is connected with a 3-way stopcock *E*, a water trap *G* and a filter pump *D*. The flask *A* is heated by an oil bath *F*, and Bunsen's burner. When the manometer shows a pressure of about 15 mm. and the thermometer a temperature between 35° and 40°, a dilute aqueous solution of hydrogen peroxide in water distils into the receiver. The temperature rises gradually to about 70° when a very concentrated solution of hydrogen peroxide remains in the distilling flask *A*. Further concentration is best effected by placing a beaker containing some of the hydrogen peroxide solution in a mixture of solid carbon dioxide and ether. The whole mass freezes. Drop a little of the frozen solid into a portion of the concentrated hydrogen peroxide solution. At between −8° to −10° small needle-shaped crystals separate. Drain away the mother liquid from the crystals, melt the crystals and cool the mass, so that another crop of crystals is obtained. Repeat the operations.

In this way, it is possible to prepare 100 per cent hydrogen peroxide The solution remaining in the distilling flask will serve for most experiments where concentrated solutions of hydrogen peroxide are required This solution can also be further concentrated by evaporation over concentrated sulphuric acid *in vacuo* This operation is conducted as follows The dish containing the mixture rests on the perforated shelf of a desiccator, Fig 79 The desiccator has a layer of concentrated sulphuric acid below the perforated shelf The lid of the desiccator, well greased, is placed in position The desiccator is then exhausted by connecting the stoppered tube with the air pump Any water vapour given off by the solution in the dish is gradually absorbed by the concentrated acid

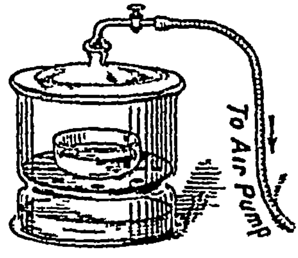


FIG 79 —Evaporation under Reduced Pressure

Concentrated hydrogen peroxide begins to attack the glass distilling flask at about 80° Wolfenstein, by changing the receiver, obtained a solution of 90 per cent hydrogen peroxide at 81°–85° at 68 mm pressure, and by repeatedly redistilling the product he got a liquid containing 99 per cent of hydrogen peroxide and boiling at 84°–85° C at 68 mm pressure

§ 5 Hydrogen Peroxide—Occurrence and Properties.

Occurrence —There is a similar uncertainty about the alleged occurrence of hydrogen peroxide in rain, snow, dew, and air as was indicated in dealing with the occurrence of ozone in air Much of the published work does not clearly discriminate hydrogen peroxide from other oxidizing substances

Properties —Pure hydrogen peroxide is a viscid liquid, colourless, when viewed in thin layers, but with a bluish tinge when viewed in thick layers The liquid has no smell Dilute aqueous solutions have a peculiar bitter metallic taste When a drop of liquid peroxide comes in contact with the skin, it forms a white blister If concentrated sulphuric acid be mixed with hydrogen peroxide at a low enough temperature to prevent heating, oxygen rich in ozone is evolved The liquid decomposes rapidly when heated at ordinary atmospheric pressures, but under reduced pressure (p 158) it can be readily distilled It boils between 68° and 69° under a pressure of about 26 mm, and at 84°–85° under a pressure of 68 mm The liquid crystallizes in needle-like prisms at −2° The liquid is soluble in water in all proportions

Pure hydrogen peroxide is fairly stable Dilute aqueous solutions keep fairly well—particularly if acid—a 3 per cent solution suffered no appreciable change when kept a year Alkaline solutions do not keep very well Impurities like silica, iron, manganese, and alumina lead to a more rapid decomposition If alcohol or ether be present, the aqueous solutions are more stable The strength of aqueous solutions is represented commercially by the number of volumes of oxygen which 100 c c of the solution will furnish on decomposition Thus 100 c c of a "10-volume solution" will give 10 volumes of oxygen when decomposed A 3 per cent. solution of hydrogen peroxide is very nearly a "10-volume solution";

a 6 per cent hydrogen peroxide solution is nearly of "20 volume" strength and so on The most concentrated solution on the market is called "perhydrol," and it contains about 30 per cent of hydrogen peroxide corresponding with a "100 volume" strength

Decomposition by contact action—Pure hydrogen peroxide is decomposed very rapidly if any dust be present A little platinum black dropped into the solution causes an explosion Similar remarks apply to finely divided gold, silver, and similar metals as well as to powdered manganese dioxide The action appears to be catalytic since the manganese dioxide, etc, remain at the end of the action unchanged in composition Charcoal or magnesium mixed with a trace of manganese dioxide ignites immediately Finely powdered iron or lead remain quiescent, but if a trace of manganese dioxide be present, the iron burns. A few drops of liquid hydrogen peroxide on a piece of cotton wool will make the cotton inflame Similar results are obtained with aqueous solutions of hydrogen peroxide but the action is much less vigorous. Rough surfaces have a disturbing effect on the stability of hydrogen peroxide—a concentrated solution is decomposed when poured on to a ground glass surface

Oxidizing properties—Hydrogen peroxide resembles ozone in its strong oxidizing qualities It liberates iodine from solutions of potassium iodide (see p 180) The reaction is accelerated by acetic and mineral acids, and particularly by ferrous sulphate. According to Schönbein one part of hydrogen peroxide in the presence of 25,000,000 parts of water can be detected by a mixture of potassium iodide and ferrous sulphate It converts lead sulphide into lead sulphate as was also the case with ozone Hence the use of hydrogen peroxide for cleaning oil paintings which have been darkened by the action of hydrogen sulphide—sometimes present in the air of towns—upon the lead compounds in the paint The brownish black coloured lead sulphide is transformed into white coloured lead sulphate. Hydrogen peroxide bleaches litmus and indigo solutions, but it does not affect mercury and silver like ozone

Dilute solutions of hydrogen peroxide are accordingly used for bleaching silk, feathers, straw, hair, ivory, teeth, etc., where more violent bleaching agents would injure the material Instead of hydrogen peroxide an acidified solution of sodium peroxide is sometimes employed. The actions are similar Since the products of the decomposition of hydrogen peroxide—water and oxygen—are harmless, it is also used medicinally as an antiseptic Hydrogen peroxide is also used in analytical work for the oxidation of sulphites to sulphates, arsenites to arsenates, chromic salts to chromates, ferrous to ferric salts, nitrites to nitrates, etc

Peroxidizing properties—Hydrogen peroxide forms peroxides of the alkalies and alkaline earths when treated with the corresponding hydroxides. For instance, with barium hydroxide $Ba(OH)_2 + H_2O_2 = BaO_2 + 2H_2O$ W Spring (1895) pointed out that hydrogen peroxide behaves in these reactions like an acid (p 139) In confirmation, if potassium or sodium carbonate be added to hydrogen peroxide the corresponding alkaline peroxide is formed and carbon dioxide is evolved $H_2O_2 + Na_2CO_3 = Na_2O_2 + CO_2 + H_2O$, on the contrary, if the hydrogen peroxide be added

to the solution of the carbonate, oxygen is evolved $2H_2O_2 + Na_2CO_3 = Na_2CO_3 + 2H_2O + O_2$. The sodium carbonate acts as a catalytic agent in the latter case

With titanium salts, hydrogen peroxide gives an orange yellow coloration supposed to be due to the formation of pertitanic acid $TiO_2 + H_2O_2 = H_2O + TiO_3$. The particular tint depends upon the amount of titanium present, and hence the reaction is used for the determination of the amount of titanium in various materials. The tint of a solution containing an unknown amount of titanium is compared with that of a similar solution containing a known quantity of titanium, and the amount in the unknown solution determined by simple rule of three. The reaction is also used as a test for hydrogen peroxide. It is said that one part of titanium in 1800 parts of water gives a deep yellow coloration, and one part in 180,000 a light yellow coloration. Cerium and vanadium salts give brick-red coloration, and uranium a bluish coloration, but these reactions are not so sensitive as with titanium salts.

With chromic acid, H_2CrO_4, hydrogen peroxide forms a blue solution which begins to decompose immediately. Some consider the oxide formed to be a compound of perchromic acid $HCrO_4$, with hydrogen peroxide, say, $HCrO_5$ (*q v*). This is pure hypothesis, no such compound has been isolated. The blue coloured peroxide, whatever it be, is much more soluble in ether than in water, so that if a mixture of chromic acid and hydrogen peroxide in a test-tube be shaken with ether, a blue ethereal solution of the peroxide will float on the surface of the aqueous layer. The compound decomposes when the ether is evaporated. This reaction is used for the detection of chromates "Add dilute sulphuric acid to the chromate solution, and shake up with ether and hydrogen peroxide. The separation of a blue ethereal layer indicates chromic acid." The necessary modification of the process for the detection of hydrogen peroxide will be obvious. It is said that this method will indicate one part of hydrogen peroxide in 80,000 parts of water

Reducing properties.—Hydrogen peroxide appears to act as a reducing as well as an oxidizing agent. With ozone it forms oxygen and water $O_3 + H_2O_2 = H_2O + 2O_2$; with silver oxide, metallic silver and oxygen $Ag_2O + H_2O_2 = 2Ag + H_2O + O_2$. The lead dioxide obtained when red lead is digested with dilute nitric acid dissolves very slowly, but if a few drops of hydrogen peroxide be added, all the lead dioxide dissolves in a few moments. The lead dioxide is reduced to lead monoxide by the hydrogen peroxide, and the product dissolves immediately in the dilute acid. This method is generally employed to hasten the solution of red lead in dilute acid prior to analysis. Hydrogen peroxide in alkaline solutions oxidizes manganese oxide, MnO, to manganese dioxide, MnO_2, but in acid solutions it reduces manganese dioxide to manganous oxide $MnO_2 + H_2SO_4 + H_2O_2 = MnSO_4 + 2H_2O + O_2$. The reducing action of the hydrogen peroxide is only apparent. According to B. Brodie (1872) the oxides of silver, manganese, etc., have an atom of oxygen which is readily disengaged from its combination. Similarly, hydrogen peroxide readily parts with its odd atom of oxygen. Consequently, the atom of oxygen in hydrogen peroxide is supposed to oxidize the odd oxygen atom in the metallic peroxide

A solution of potassium permanganate—$KMnO_4$—acidified with sulphuric acid is rapidly reduced by hydrogen peroxide $5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$. Consequently, if an aqueous solution, containing a known amount of potassium permanganate, be run from a burette into a known volume of hydrogen peroxide until the pink colour of the permanganate is no longer discharged, it follows, from the equation, that every two molecules of $KMnO_4$ correspond with five molecules of H_2O_2, or $2 \times 158{\cdot}02$ (the molecular weight of $KMnO_4$) grams of potassium permanganate correspond with $5 \times 34{\cdot}02$ (the molecular weight of H_2O_2) gram of hydrogen peroxide, otherwise expressed, 1 gram of potassium permanganate represents 0·5382 gram of hydrogen peroxide

EXAMPLE —45 c c of a standard solution of potassium permanganate containing 20 grams of $KMnO_4$ per litre were decolorized by 25 c c of a solution of hydrogen peroxide What amount of H_2O_2 is present in a litre of the hydrogen peroxide? Here 1000 c c of the standard solution contain 20 grams of $KMnO_4$, hence, 1 c c contains 0·02 gram, or 45 c c contain 0·9 gram But from the equation, 1 gram of $KMnO_4$ represents 0·5382 gram of H_2O_2, hence, 25 c c. of hydrogen peroxide has $0{\cdot}5382 \times 0{\cdot}9 = 0{\cdot}4844$ gram of H_2O_2. Hence a litre will have 19·4 grams of H_2O_2

Qualitative tests for the detection of hydrogen peroxide—Special attention may be called to the titanium sulphate test, the chromic acid test, the potassium iodide test, and the methods for distinguishing ozone from hydrogen peroxide

§ 6 Hydrogen Peroxide—Composition and Constitution

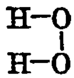
1 **Empirical formula**—J Thénard (1818) introduced a weighed amount of the peroxide in a small vial into a graduated cylinder over mercury The vial was broken and its contents decomposed either by introducing manganese dioxide, or by heat. 17 parts of hydrogen peroxide by weight gave nearly 8 parts by weight of oxygen, and $17 - 8 = 9$ parts by weight of water Otherwise expressed, 34 parts of hydrogen peroxide give 18 parts of water and 16 parts of oxygen Hence the peroxide contains hydrogen and oxygen in the proportion of 2 atoms of hydrogen 2 atoms of oxygen The simplest formula for hydrogen peroxide is therefore HO There is here nothing to show whether HO or some multiple of HO, say H_nO_n, is the proper formula for the compound, since the latter has the same percentage composition as the former

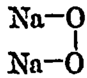
2 **Molecular formula.**—The instability of hydrogen peroxide prevents a determination of its vapour density being made in the regular manner The molecular weight can be determined by the "freezing point method" which will be described later The result is nearly 34. This agrees with the formula H_2O_2—the generally accepted value

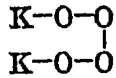
3 **Constitutional or graphic formula**—The formation of hydrogen peroxide by the action of oxygen on hydrogen, as the latter is liberated during the electrolysis of water, might lead to the supposition that its formula is HO–OH (or HO≡OH) Hence, by analogy, it might be supposed that the peroxides are similarly constituted NaO–ONa, etc. There is no adequate reason for assigning to hydrogen peroxide a constitution other than HO–OH, although Bach advocates $\substack{H \\ H}\!>\!O{=}O$

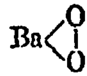
D I Mendeléeff subdivides the peroxides into two classes depending upon the valency of the element united to the oxygen atoms —

1 Superoxides —Those peroxides in which the oxygen atom or atoms, over and above those required to form the basic oxide, are *singly linked* to the metal and to the other oxygen atoms, so as to form a chain The valency of the metal is the *same* in the peroxide as in the basic oxide *E g*


Hydrogen peroxide

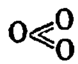

Sodium peroxide

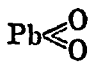

Potassium tetroxide


Barium peroxide

The superoxides are often called peroxidates, being regarded as "salts" of hydrogen peroxide (p 196)

2 Polyoxides —Those peroxides in which the oxygen atom or atoms, over and above those required to form the basic oxide, are *doubly linked* to the metal so that the valency of the metal in the peroxide is *greater* than the valency of the metal in the basic oxide. *E g* :


Ozone


Lead peroxide


Manganese peroxide

These oxides possess feeble basic or feeble acidic properties—possibly both

The superoxides which yield hydrogen peroxide when treated with water or a dilute acid are probably constituted like hydrogen peroxide Thus sodium peroxide with hydrochloric acid gives hydrogen peroxide, and potassium tetroxide, which gives oxygen and hydrogen peroxide, is probably constituted on the same plan The polyoxides are not usually attacked by dilute acids Both types with concentrated sulphuric acid evolve oxygen The mechanism of the reaction is probably different in the two cases With the superoxides, hydrogen peroxide is probably formed as an intermediate product $BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$; followed by $2H_2O_2 = 2H_2O + O_2$ With manganese peroxide $2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$ Similarly with hydrochloric acid, both give chlorine, but with the superoxides, hydrogen peroxide is first formed, and this reacts with the excess of acid forming chlorine: $2HCl + H_2O_2 = 2H_2O + Cl_2$, with the polyoxides, on the other hand, an intermediate perchloride can often be detected—with manganese dioxide, probably $MnCl_3$, and with lead peroxide, $PbCl_4$ is formed [1]

§ 7 Thermochemistry

It was convenient, in a preceding paragraph, to resolve matter, as we know it, into two abstractions—matter and energy Neither exists

[1] Attempts have been made to show that two of the best known "polyoxides," PbO_2 and MnO_2, are differently constituted because lead dioxide when exposed to sulphurous acid, H_2SO_3, furnishes lead sulphate, $PbSO_4$, while manganese dioxide furnishes manganous dithionate, MnS_2O_6 It is more probable that the action in both cases is similar, manganese dioxide forming the normal sulphite $Mn(SO_3)_2$, and lead dioxide the basic sulphite $PbO\,SO_3$ Both salts then undergo internal rearrangement, the former producing a dithionate, and the latter a normal sulphate

alone We have no acquaintance with the one apart from the other Isolated, matter and energy are pure abstractions Each one completes and presupposes the other The element phosphorus, for instance, must be regarded as a form of matter which is always associated with a certain amount of available energy, because it is able to do chemical work, and we cannot conceive of energy coming from nothing We cannot answer How much energy is associated with the phosphorus? The actual amount available possibly depends upon the nature of the substance with which it is brought in contact Similarly with oxygen When these two elements—oxygen and phosphorus—are brought in contact, under the right conditions for the degradation of energy, chemical action sets in, and the chemical energy is degraded or transformed into heat or light The resulting compound—phosphorus pentoxide—still contains some chemical energy, for if it be mixed with water, a great amount of heat is developed, chemical energy is degraded, and phosphoric acid results. The phosphoric acid still contains chemical energy because more energy is degraded in the form of heat when the phosphoric acid is brought into contact with sodium hydroxide Every chemical reaction involves a change both in the form of the matter and in the form of the energy of the system What is generally understood by "descriptive" or "material" chemistry deals with the former, not with the latter Chemistry proper is essentially concerned with both energy and matter

Law of Lavoisier and Laplace—The free or available chemical energy of different substances is usually degraded in the form of heat during chemical action The system gets hotter because heat is evolved by the reacting substances—such reactions are said to be *exothermal reactions* in contrast with *endothermal reactions* which absorb heat and thus cause the system to become cooler (That branch of chemistry which deals with the relation between thermal and chemical energy is called thermochemistry) Experiment shows that every compound has a definite heat of formation, which is numerically equal to the heat required for the decomposition of the compound back into its elements, but of opposite sign If it were not so, heat would be gained or lost when a compound is formed and then decomposed back into its original constituents. Such a result is at variance with the principle of the persistence or conservation of energy The fact that every compound has a definite heat of formation which is numerically equivalent to its heat of decomposition but of opposite sign, is sometimes called the law of Lavoisier and Laplace, because A. L. Lavoisier and P S de Laplace first pointed out this generalization between 1780–84.

The symbols used in thermochemistry—It will be remembered that in physics, the unit of heat is the calorie, and a calorie represents the amount of heat required to raise the temperature of one gram of water through 1° C Consequently, 100 cals will raise the temperature of 100 grams of water 1°, or of 1 gram of water 100° In chemistry, it is convenient to represent the thermal value of a reaction by reference to the formula weights of the substances concerned in the reaction Thus the heat of formation of phosphorus pentoxide is 370,000 cals This means that 370,000 cals are generated when 142 grams of phosphorus pentoxide are formed by burning 62 grams of phosphorus in oxygen To avoid dealing with large

numbers it will be more convenient to consider a **Calorie** as the amount of heat required to raise the temperature of 1000 grams of water 1° C This is the so called "kilogram-calorie" or the "big calorie," and it is here written with a capital "C" Thus "cal" refers to the gram-calorie, "Cal" refers to the kilogram calorie Hence the energy degraded in the form of heat when phosphorus burns in oxygen is equivalent to 370 Cals. This is represented in symbols

$$2P + 5O = P_2O_5 + 370 \text{ Cals}$$

If the states of aggregation of the initial and final products of the reaction are not self-evident, the states of aggregation must be represented in the equation, otherwise latent heats of fusion or vaporization may lead to ambiguity[1] Thus

$$2H + O = H_2O_{gas} + 59\ 4 \text{ Cals}$$

means that the union of 2 grams of hydrogen with 16 grams of oxygen is attended by the evolution of 59 4 big calories when the water produced is in the form of steam, if the steam is condensed to a liquid,

$$2H + O = H_2O_{liq} + 68\ 4 \text{ Cals}$$

The extra 9 0 Cals represents the heat given out when 18 grams of steam are condensed to a liquid Again, if the reacting substances are in aqueous solution, a certain amount of heat may, or may not, be dissipated in the act of solution For example, 13 7 Cals are evolved when a dilute solution of sodium hydroxide is mixed with a dilute solution of hydrochloric acid The dilute solution is represented by a suffix "aq" Thus,

$$NaOH_{aq} + HCl_{aq} = NaCl_{aq} + H_2O + 13{\cdot}7 \text{ Cals}$$

If the sodium chloride were prepared by passing hydrogen chloride gas into a dilute solution of sodium hydroxide, more heat is evolved, because 17 4 Cals are evolved when 36 4 grams of hydrogen chloride are dissolved in water

$$NaOH_{aq} + HCl_{gas} = NaCl_{aq} + H_2O + 31\ 1 \text{ Cals}$$

Some disturbing effects—Again, the chemical and physical condition of the reacting substances must be taken into consideration The heats of combination of hydrogen in oxygen and in ozone would not be the same because of the reaction $2O_3 = 3O_2 + 68\ 2$ Cals Allowance would have to be made for this extra energy associated with ozone

It is necessary to distinguish clearly between the observed heat changes and the real heat changes due to the degradation of chemical energy as heat The observed thermal value of a reaction may be greater or less than that which corresponds with the chemical energy actually degraded during a given chemical reaction For example, suppose that we start with a mixture of two volumes of hydrogen and one volume of oxygen, and finish with liquid water, there is a tremendous contraction in volume This contraction occurs under atmospheric pressure (76 cm mercury) Hence the atmosphere does work *on* the system, and that work appears as heat which raises the temperature of the system, and makes the observed heat of combination appear greater than it really is The work can easily be calculated,[2] and it is equivalent to 0 9 Cal Hence

[1] Some represent gases by means of italics, solids by clarendon type, and liquids by ordinary type

[2] One gram molecule of steam occupies 22 3 litres The gases from which the steam was formed occupied 1½ times this volume, *i e* 33 45 litres A column of

Apparent energy degraded in reaction	69 3 Cals
Energy due to contraction	0 8 Cal
Energy actually due to reaction	68 5 Cals

Heat may also appear to be generated during a chemical reaction which is partly due to differences in the specific heats of the initial and final products of the reaction If the latter be less than the former, some of the heat generated will be due to this fact, and not to the degradation of chemical energy

§ 8 The Principle of Maximum Work

The heat developed during a reaction represents a certain amount of potential energy which was associated with the atoms in some way, we are therefore much tempted to generalize, as Thomsen did in 1853, and assume that the thermal value of a reaction is a measure of chemical affinity between the reacting substances, and that every chemical change which can take place without the aid of external energy will be accompanied by the evolution of heat, or as M. Berthelot expressed it in 1869 **Every chemical change which takes place without the aid of external energy tends to the production of that which is accompanied by the development of the maximum amount of heat** This is the so called *principle of maximum work* Hence also reactions which proceed spontaneously, when once they have been started, liberate some form of energy, generally heat, during the progress of the reaction

Objections —There are three main objections to this generalization which cannot therefore be true in its present form

(1) In balanced reactions (p 97), the reaction may be exothermal in one direction, and endothermal in another According to the principle of maximum work, the exothermal reaction ought to go completely to an end Hence the principle is not in agreement with facts

(2) Many reactions are known to be accompanied by an absorption of heat

(3) Many systems require a preliminary impulse (p 112) to start the reaction, and hence it would be necessary to introduce a clause to provide for this phenomenon

The principle of maximum work must therefore be either amended or abandoned Further investigations have shown that probably all possible chemical and physical reactions will be exothermal and complete at absolute zero, $-273°$, and consequently, the principle of maximum work will probably apply at that temperature At ordinary temperatures, the principle is only roughly applicable

§ 9 The Principle of Reversibility

The most stable compounds are usually, but not always, those with the greatest heat of formation In a general way, the higher the temperature the less the stability of exothermal compounds, and conversely,

mercury, 1 sq cm sectional area and 76 cm long weighs $76 \times 13\ 59 = 1033$ grams (since the specific gravity is 13 59) This pressure exerted along a path of 33 45 cm will be $33\ 45 \times 1033$ gram cms, or, $33\ 45 \times 1\ 033$ kilogram cms But 42 65 kilogram cms. are equivalent to one calorie Hence, $33\ 45 \times 1033 \div 42\ 65 = 800$ cals or 0 8 Cal

endothermal compounds generally become more stable at higher temperatures because an absorption of heat is necessary for their formation. Here, then, we have another illustration of "the principle of reversibility" previously discussed, p 25 A compound formed by an evolution of heat is decomposed by the addition of heat, and a compound formed by an absorption of heat is decomposed by the withdrawal of heat. W Ostwald (1891) has said.

It is generally believed that at a high temperature, such as that which exists in the electric arc, and in the sun's atmosphere, all compounds must be dissociated into their elements This view is certainly not justified On the contrary, what we actually know about the stability of compounds is that all compounds which are formed with an absorption of heat become more stable with rising temperatures, and *vice versa* Owing to the fact that the majority of compounds known to us are formed from their elements with the evolution of heat, and in consequence, become more unstable as the temperature rises, it has been concluded that this is generally the case But if we remember that acetylene and cyanogen—two compounds formed with the absorption of heat—are readily formed in quantity at the high temperature of the blast furnace, and in the arc light, we see the possibility that spectra occurring at high temperatures may belong to compounds which exist only at elevated temperatures

As a matter of fact, some endothermal compounds become exothermal at higher temperatures—*e g* hydrogen iodide, hydrogen sulphide, and probably ozone, hydrogen peroxide, silver oxide, etc Conversely, some exothermal compounds become endothermal at higher temperatures—*e g* silicon hexachloride Consequently, there may be a reversion in the thermal value of some chemical processes when the temperature is augmented The consequence is that a compound may be unstable at low temperatures and stable at higher temperatures, or conversely, stable at a low temperature and unstable at a higher temperature Hydrogen peroxide and ozone are examples of the former, water an example of the latter.

§ 10 Hess' Law

G H. Hess (1840) measured the heat developed during the formation of a compound made in several different ways and came to the conclusion that the amount of heat evolved during the formation of a given compound is the same whether the compound is formed directly or in a series of intermediate stages This is called Hess' law The principle may be illustrated by making calcium chloride by the action of quicklime on dilute hydrochloric acid. It is found that

$$CaO + 2HCl_{aq} = CaCl_2aq + H_2O + 46 \text{ Cals}$$

Instead of this, first slake the quicklime, and

$$CaO + H_2O = Ca(OH)_2 + 15 \text{ Cals}$$

Dissolve the calcium hydroxide in water, and

$$Ca(OH)_2 + Aq = Ca(OH)_2aq + 3 \text{ Cals}$$

Mix the lime water with dilute hydrochloric acid, and

$$Ca(OH)_2aq + 2HCl_{aq} = CaCl_2aq + H_2O + 28 \text{ Cals}$$

These three steps in the formation of the solution of calcium chloride give a total 28 + 3 + 15 = 46 Cals as the heat of formation The same result was obtained by the direct action of the dilute acid on quicklime,

The heat of formation of a compound is independent of its mode of formation

This result is but a particular application of the law of persistence of energy and it may be expressed by saying that the change of energy of a system in passing from one state to another depends upon the initial and final states of the system, and not on the intermediate states. Starting with given raw materials, suppose that it were possible to make a compound by two different processes so that the total heats of formation of the compound were different, it follows that a decomposition of the compound formed by one of the processes (Lavoisier and Laplace's law) could lead to the creation or destruction of energy

It follows from Hess' law that if the heat of formation of carbon dioxide be $C + 2O = CO_2 + 94\ 3$ Cals., and $CO + O = CO_2 + 68$ Cals, we have

$$(C + 2O) - (CO + O) = 94\ 3 - 68 \text{ Cals.}$$

Consequently, the heat of formation of carbon monoxide is $C + O = CO + 26\ 3$ Cals. This illustrates the fact that **the thermal value of a reaction is the sum of the heats of formation of the final products of the reaction less the heats of formation of the initial products of the reaction** This corollary to Hess' law is valuable because it enables the heat of formation of a compound from its elements to be computed when a direct determination is either impracticable or very difficult.

✓ EXAMPLE —It is required to compute the heat of formation of $K + Cl = KCl$, when it is known that the heat of formation of $K + O + H + Aq = KOH_{aq}$ $+ 116\ 5$ Cals, $2H + O = H_2O_{liq} + 68\ 4$ Cals, $H + Cl = HCl_{aq} + 39\ 3$ Cals, heat of solution of KCl in water—4 4 Cals, and that

$$KOH_{aq} + HCl_{aq} = KCl_{aq} + H_2O + 13\ 7 \text{ Cals}$$

This last relation can be written

$$(K + Cl + Aq) + (2H + O)_{liq} - (H + Cl + Aq) - (K + O + H + Aq) = -13\ 7 \text{ Cals}$$

Consequently, after substituting the given data, we get

$$(K + Cl + Aq) + 68\ 4 - 39\ 3 - 116\ 5 = -13\ 7$$

Hence,

$$K + Cl + Aq = KCl_{aq} + 73\ 7 \text{ Cals.}$$

Subtract the heat of solution $-4\ 4$ Cals, and we get $73\ 7 - (-4\ 4) = 78\ 1$ Cals for the thermal value of the reaction $K + Cl = KCl$ It will be noticed that the solution of potassium chloride in water is an endothermal process, and hence the heat of formation of KCl_{aq} is less than the heat of formation of KCl

Questions

1 Write an account of the chemistry of ozone In what way is the composition of ozone deduced?—*St Andrews Univ*

2 Finely divided silver thrown into hydrogen dioxide occasions a sudden evolution of oxygen, but the metal is not oxidized Silver oxide in like manner occasions a similar evolution, and metallic silver results Explain these facts —*Science and Art Dept*

3 What are the chief properties of hydrogen peroxide? 20 c c of a solution of this substance, after acidification with dilute sulphuric acid reduced 24 c c of $\frac{1}{10}$ N potassium permanganate Calculate the percentage of hydrogen peroxide in the solution —*St Andrews Univ*

4 What is meant by the terms "endothermic" and "exothermic" compounds? To what class do substances known as 'explosives belong"? Account for the greater activity of ozone over that of oxygen on thermochemical grounds, and for its resolution into oxygen by compression —*Science and Art Dept*

5 What is a 'silent discharge"? Make a sketch of a piece of apparatus suitable for submitting gases to such discharge, and indicate any chemical changes which can be produced by its means —*London Univ*

6 What is the heat of formation of zinc chloride, $ZnCl_2$, in solution when the reaction, $Zn + 2HClaq = ZnCl_2aq + H_2 + 34.4$ cals, and the heat of formation of an aqueous solution of hydrogen chloride, is given by the equation $H_2 + Cl_2 = 2HCl + 78.6$ cals ?—*French Coll*

7 Discuss the question of the valency of oxygen referring specially to the evidence of its character as a quadrivalent element —*Board of Educ*

8 Five cubic centimetres of a solution of hydrogen peroxide were mixed with an acidified solution of potassium permanganate and 20 c c of oxygen were evolved measured at N T P From this result, calculate the per cent of hydrogen peroxide present in the solution. How would such a solution be labelled in commerce ?—*Board of Educ*

9 When hydrogen is heated to 2100°, it has been stated that some of the diatomic molecules are decomposed $H_2 \rightleftharpoons 2H$, again ozone is formed when oxygen is subjected to an electric discharge $3O_2 \rightleftharpoons 2O_3$ Are the substances symbolized by O_2, H_2, and O_3 elements ? How do the facts just indicated affect the definition of an element An element is a substance which cannot be separated into simpler substances by any known means ?

10 How may a chemical equation be modified so as to represent not only a redistribution of matter but also a redistribution of energy ? Explain what is meant by the fact of formation of a compound From the following data find the heat of formation of acetylene, C_2H_2: When 24 grms of carbon, 2 grms of hydrogen, and 26 grms of acetylene are burnt separately in an excess of oxygen, *194,000, 68,000, and 310,000 calories are respectively evolved* —*Cape Univ*

11 Find the amount of heat K liberated in the reaction $AlCl_3 + 3Na = 3NaCl + Al + xK$ The heat of formation of aluminium chloride, $AlCl_3$, is $1610K$, and of sodium chloride, NaCl, $976K$ —*Sydney Univ*

12 What amount of heat is evolved when 46 grms of metallic sodium reacts with an excess of water, given the heats of formation of water (H_2O) is 69 Cals, and of sodium hydroxide (NaOH), 112.5 Cals ?

13 What substances besides ozone have the power of turning iodized starch paper blue ? How are they distinguished from ozone ?—*Science and Art Dept*

14 Write a concise historical account of the chemistry of ozone as developed by the researches of Schonbein Andrews and Tait, Brodie, Soret, Hautefeuille and Chappuis, Houzeau, and others How do you account for ozone being an explosive substance under certain conditions ? Define the conditions under which it may be exploded —*Science and Art Dept*

15 Find the heat of formation of aldehyde, C_2H_4O from its elements when aldehyde is (*a*) liquid, and (*b*) gaseous Data $C_2H_4O + 5O = 2CO_2 + 2H_2O$, $[C_2H_4O, 5O]$ liquid 275.5 Cals, $[CO_2]$ 96.6 Cals, $[H_2O]$ liquid 68.4 Cals, $[H_2,O]$ gaseous 58.7 Cals, $[C_2H_4O,5O]$ gaseous, 266.0 Cals —*Owens College*

CHAPTER XII

OSMOTIC PRESSURE AND RELATED PHENOMENA

§ 1 Diffusion in Gases and in Liquids

The substitution of analogy for fact is the bane of chemical philosophy; the legitimate use of analogy is to connect facts together and to guide to new experiments —H DAVY

LET a large crystal of a coloured salt—say copper sulphate—be placed at the bottom of a tall glass cylinder, and the remainder of the jar be filled with water The coloured salt is chosen because the movements of the resulting solution can be readily seen Let the jar stand where it will not be disturbed by evaporation, agitation, etc The surface of separation between the solid and solvent will be gradually obliterated, in time, the coloured salt will diffuse uniformly throughout the whole body of liquid. The diffusion of the salt in the solvent seems to be analogous with the process of diffusion in gases It is inferred that the molecules of the liquid are in perpetual motion in all directions, and that the protracted time occupied by the diffusion of the molecules of the dissolved salt in the liquid is due to the close packing of the molecules of the liquid. Consequently, the free progress of the molecules of the dissolved salt—p 114—in the solvent is greatly impeded.

Just as the molecules of a gas in a closed vessel are disseminated in a relatively large space, so are the molecules of a solid in solution scattered in a relatively large volume of solvent It is true that the molecules of the salt in solution could not occupy the space if the solvent were absent, otherwise the analogy between a substance dissolved in a solvent and a gas scattered in space would be very close Arguments from analogy are notoriously treacherous, and whatever conclusions might be inferred from a closer study of the analogy between the process of solution and gaseous diffusion, the fact that the molecules of the dissolved substance are co mingled with the solvent, and that the molecules of the gas are not associated with such an agent must be constantly borne in mind As G F Fitzgerald has said "The dynamical condition of molecules in solution is essentially and utterly different from that of the molecules of a gas"

§ 2 Solution Pressure—Osmotic Pressure

If the diffusion of gases be resisted by placing a permeable partition between two gases, a pressure will be exerted upon the partition as was exemplified in the experiments on p 106 It is easy to show that the particles of a dissolved substance exert a similar pressure when a partition

is placed between the solution and solvent so that the partition offers no obstacle to the free circulation of the molecules of the solvent, but resists the free passage of the molecules of the dissolved substance

A piece of wet bladder is stretched and wired over the head of a wide thistle-headed funnel with a stem about 10 cm long When nearly dry, the bladder is removed and the hot funnel is smeared about the rim with marine glue The bladder is immediately wired securely in position The thistle-headed funnel is nearly filled with a concentrated solution of cane sugar and joined by means of pressure tubing or a rubber stopper with a piece of capillary tubing of ½ mm bore bent S shaped as indicated in Fig 80 The funnel is immersed in a jar of water The level of the index of coloured water in the capillary tube is marked with gummed paper and the apparatus is allowed to stand over night In the morning the liquid in the capillary will have risen about 10 cm. Water has obviously passed from the beaker through the membrane into the sugar solution.

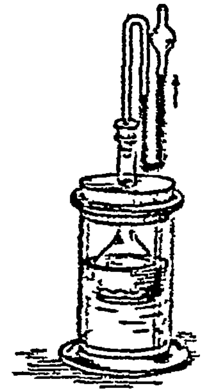


Fig 80 —Illustration of Osmotic Pressure

The passage of water through a membrane in this manner is called osmosis—*from the Greek ὠσμός (osmos), a push* If *the osmosis be inwards towards the solution it is called* endosmosis, *if outwards* exosmosis. The membrane permeable to the solvent impermeable to the dissolved substance, is called a semipermeable membrane The extra pressure exerted upon the membrane by the sugar solution was styled by W Pfeffer (1877), "the osmotic pressure of the sugar solution" Solutions with the same osmotic pressure are said to be *is-osmotic* or isotonic

The action is curious In the ordinary nature of things the sugar would diffuse into the solvent until the whole system had one uniform concentration The membrane prevents this. If the sugar cannot get to the solvent, the solvent goes to the sugar—a case of Mohammet and the mountain Molecules of sugar and molecules of water attempt to pass through the membrane; the way is open for the molecules of water, but not for the molecules of sugar Water can pass freely both ways The extra pressure on the solution side of the membrane—the solution pressure—is supposed to be due to the bombarding of the membrane by the molecules of sugar Equilibrium occurs when the number of molecules of water passing downwards through the membrane is equal to the number passing in the opposite direction. The resulting pressure is the solution pressure or the osmotic pressure of the solution

Let us be perfectly clear about this or we may be led *into error* The fact observed is that the osmotic pressure is the excess of the pressure on the solution side of a semipermeable membrane over the pressure on the solvent side. The hypothesis here suggested—often styled van't Hoff's hypothesis—is that this pressure is due to the bombarding of the semipermeable membrane by the dissolved molecules trying to diffuse into the solvent and make solvent and solution one uniform concentration

Imagine the experiment arranged a little differently Suppose the aqueous solution of sugar in the lower part of a cylinder, Fig 81, to be separated from the pure solvent in the upper part of the cylinder by a semipermeable membrane *A* so fitted that it can slide freely up and down

the cylinder The upward osmotic pressure of the solution will naturally force the piston upwards, and a weight p, equivalent to the osmotic pressure of the solution, will be required to keep the semipermeable membrane in one fixed position C Brown has an interesting experiment illustrating this A concentrated solution of calcium nitrate is saturated with phenol and the mixture poured into a tall narrow cylinder The excess of phenol rises and floats upon the surface of the calcium nitrate solution The phenol should not be in larger excess than is required to give a layer a few millimetres thick. Distilled water, saturated with phenol is carefully poured above the two layers of liquid in the cylinder The water floats on the surface of the phenol The water on both sides of the phenol can traverse the partition of phenol, but the calcium nitrate cannot pass through Hence the layer of phenol is a semipermeable membrane Mark the level of the layer of phenol in the cylinder by means of a piece of gummed paper If the upward motion of the layer of phenol be marked from day to day, it will be found to rise higher and higher, and finally surmount the rest of the liquid in the cylinder

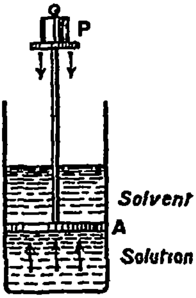


FIG 81 —Osmotic Pressure

§ 3 The Measurement of Osmotic Pressure

Animal membranes are objectionable when exact measurements are required because, to a certain extent, the results depend upon the nature of the membrane, the membrane is not strong enough to withstand the great pressures developed by osmosis, and, most serious of all, the membrane is not quite semipermeable, an appreciable amount of, say, sugar does actually pass through the membrane It would therefore be as profitable to measure the pressure of a gas in a leaking vessel as to try to measure the osmotic pressure of a solution with a membrane which allows part of the dissolved substance to pass through We therefore fall back on artificially prepared membranes No artificial membrane has been so successful as a film of copper ferrocyanide deposited[1] between the inner and outer walls of a "porous pot," and illustrated by the sketch of a broken pot, *A*, Fig 82 The porous pot with its semipermeable membrane *A* is fitted with a suitable manometer (Fig 83) to indicate the pressure W Pfeffer made some measurements with cells made in this manner, in 1877 The apparatus was immersed in a large bath of water to maintain the temperature constant during the experiment.

FIG 82 —Semipermeable Membranes.

§ 4 Osmotic Pressure and the Gas Laws

1 **The relation between osmotic pressure and the concentration of the solution—Boyle's law**—W Pfeffer (1877) obtained some data

[1] By steeping a clean porous pot in an aqueous solution of potassium ferrocyanide, rinsing in water, and then submerging the pot in an aqueous solution of copper sulphate

with this apparatus which J H van't Hoff (1887) utilized, with remarkable cleverness in developing what he called "the *rôle* of osmotic pressure in the analogy between solutions and gases" The experimental data showed that the osmotic pressure is very nearly proportional to the concentration of the solution, otherwise expressed, the osmotic pressure appears to depend upon the degree of crowding of the molecules of the dissolved substance Instead of repeating Pfeffer s measurements, some later determinations by H. N Morse (1907) can be quoted (temperature nearly 0°)

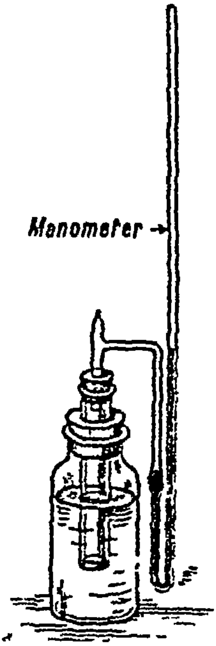


FIG 83 —Measurement of Osmotic Pressure

Concentration	0 1,	0 2,	0 3,	0 4,	0 5,	0 6,	1 0[1]
Osmotic pressure	2 4,	4 7,	7 0,	9 3,	11 7,	14 1,	23 7 atm
Equivalent gas pressure	2 2,	4 5,	6 7,	8 9,	11 1,	13 4,	22 3 atm

The "equivalent gas pressure" is here calculated on the assumption that a "sugar gas' obeying Boyle's law really exists The results are plotted in Fig 84 The deviation of the osmotic pressure curve from the dotted curve emphasizes the fact that the deviations of the osmotic from the equivalent "gas pressures" grow larger with increasing concentrations, and hence exact proportionality occurs only when the solutions are very dilute For dilute solutions, the osmotic pressure is nearly proportional to the concentration, or, as W Ostwald puts it, "the osmotic pressure of a sugar solution has the same value as the pressure the sugar would exert if it were contained, *as a gas*, in the volume occupied by the solution" This is another way of saying that the relation between the osmotic pressure of a solution and its concentration has the same form as Boyle's law for gases The analogy does not work out so well for concentrated solutions as with dilute solutions—possibly owing to the disturbing effects of overcrowding produced by (1) molecular attraction between the molecules of the dissolved substance, (2) and between the molecules of the solute and solvent, and (3) the volumes of the molecules themselves The first and last of these effects for gases were discussed when dealing with Boyle's law for gases

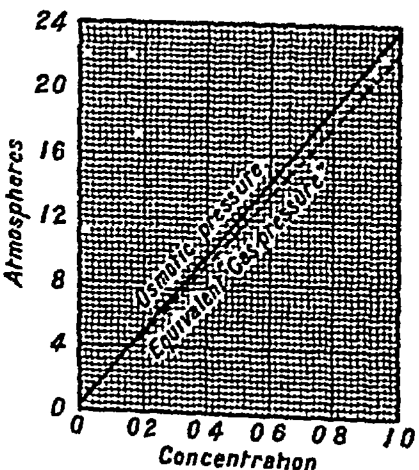


FIG 84 —Osmotic Pressure and Concentration

2 The relation between osmotic pressure and temperature—Charles' law—Pfeffer's measurements on the influence of temperature also showed that the osmotic pressure is proportional to the absolute

[1] Morse's data are here rounded off, and only a few selected One molecule weight of glucose expressed in grams will occupy 22 4 litres (p 60) Hence

temperature, which means that the relation between the osmotic pressure and the temperature of a given solution has a formal analogy with Charles' law for gases In illustration, some results by H N Morse (1911) for unit concentration may be quoted

Temperature	0°	5°	10°	15°	20°	25°
Osmotic pressure	24 8,	25 3,	25 7,	26 2,	26 6,	27 0 atm
Equivalent gas pressure	22 2,	23 0,	23 4,	23 8,	24 2,	24 5 atm

The "equivalent gas pressure" is here calculated on the assumption that a "sugar gas" obeying Charles' law really exists These numbers are plotted in Fig 85, and the graphs show the proportionality between osmotic pressure and temperature, p/T = constant The space between the two curves represents the deviation of the observed osmotic pressure, from the pressure calculated on the assumption that the dissolved substance behaves as if it were a gas

3 **Avogadro's hypothesis applied to solutions**—By a comparison of the concentration of solutions at the same temperature and the same osmotic pressure, it has been inferred that they contain the same number of molecules of the dissolved substance per unit volume The term "number of molecules" is used in the same sense that the term is used in stating Avogadro's hypothesis for gases "Equal volumes of all gases at the same temperature and pressure contain the same number of molecules" Hence van't Hoff's hypothesis assumes that *the osmotic pressure and related properties—vapour pressure, freezing point, and boiling point—of dilute solutions* (1) *depend upon the number*[1] *of molecules of solute dissolved in unit volume of the solution, and* (2) *are independent of the chemical nature of the solvent and solute, and* (3) *of the relations between solvent and solute*

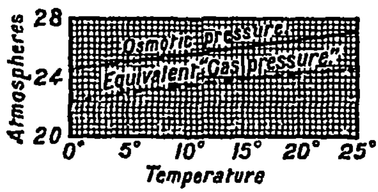


FIG 85 —Osmotic Pressure and Temperature

Equal volumes of solutions containing the same number of solute molecules have the same osmotic pressure There is a striking resemblance between this assumption and Avogadro's hypothesis for gases, and it harmonizes with a number of facts The principle can be applied to measure the molecular weight of substances in solution

EXAMPLES —(1) An aqueous solution of 1 0047 grams of orthoboric acid per litre at 0° has an osmotic pressure of 27 3 cm of mercury What is the molecular weight of the acid? Since 1 gram molecule of a substance in the gaseous state occupies 22 3 litres at 0° and 760 mm, we have here to find what weight of substance will occupy 22 3 litres at 0° and 760 mm, given 1 0047 gram occupy 1 litre at 0° and 273 mm pressure Obviously, 1 0047 gram will occupy 0 361 litre at 0° and 760 mm, and if 0 361 litre weighs 1 0047 gram, 22 3 litres will weigh 62 grams at the same temperature and pressure Hence the molecular

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0 1 molecule will occupy 2 23 litres By choosing the concentration so that in Boyle's relation pv = constant, a solution containing a molecular weight expressed in grams per 22 3 litres, has a concentration of 22 3 units when $p = 1$, we get from Boyle's law $p - C = 22\ 3$ The concentration, it will be remembered is inversely proportional to the volume Hence for a concentration 0 1, we get $p = 2\ 23$, for $C = 0\ 2$ $p = 4\ 46$, etc

[1] COLLIGATIVE PROPERTIES —In contradistinction to additive properties, colligative properties depend on the relative number of molecules present and not on the kind of molecules—*e g* the freezing and boiling points of solutions

weight of the given acid is 62, this agrees with the formula $B(OH)_3$ for orthoboric acid

(2) A 2 per cent solution of cane sugar has an osmotic pressure of 1016 mm at 15°, what is the molecular weight of cane sugar? 100 c c at 1016 mm pressure becomes 0 126 litre at 760 mm pressure and 0°, and 0 126 litre corresponds with 2 grams of cane sugar Hence 22 3 litres will have 355 grams at the same temperature and pressure The molecular weight of cane sugar is therefore 355 The true number is 342

There are so many experimental difficulties involved in the direct measurement of osmotic pressures that the method is rarely if ever employed for molecular weight determinations

§ 5 The Relation between the Vapour Pressure of a Solution and the Molecular Weight of the Solute.

M. Faraday knew in 1822, that the vapour pressure of a solution is lower than the vapour pressure of the pure solvent, but A Wullner discovered the important fact experimentally, in 1858 that the lowering of the vapour pressure of a solution is proportional to the quantity of substance in solution provided that the dissolved substance is non-volatile This is sometimes called Wullner's law

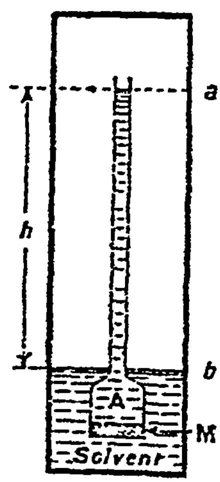

FIG 86

Suppose a solution A, Fig 86, confined in a long stemmed tube, as illustrated in the diagram, be separated by a semipermeable membrane M from the pure solvent Let all be confined in a closed vessel Osmotic pressure will force the solution to rise in the narrow tube to a height h, when the whole system is in equilibrium Let p_s denote the vapour pressure of the solution in the narrow tube, and p the vapour pressure of the solvent in the outer vessel The vapour pressure of the solution at the surface in the narrow tube must be equal to the vapour pressure of the solvent at the same level, otherwise distillation would take place either to or from the surface of the liquid in the narrow tube In either case there would be a constant flow of liquid respectively to or from the vessel A through the semipermeable membrane in order that h may have a constant value Otherwise expressed, perpetual motion would occur By the "law of excluded perpetual motion" this is impossible, hence the vapour pressure of solution and solvent at the upper level of the solution in the narrow tube must be the same The vapour pressure of the solvent at the level a will be equal to the vapour pressure of the solvent at the lower level b less the pressure of a column of vapour of height h per unit area, or $p=p_s+w$ Since the height h is determined by the osmotic pressure, which in turn is determined by the concentration of the solution, there must be a simple proportionality between the osmotic pressure or concentration of the solution and the lowering of the vapour pressure $(p-p_s)$ Just as the osmotic pressure of a dilute solution is proportional to the concentration of the dilute solution, so it can be proved that the vapour pressure is proportional to the osmotic pressure, and consequently, the relative lowering of the vapour pressure of a solvent by the

addition of a foreign substance is proportional to the concentration The phenomenon can be illustrated by introducing about 2 c c of water, 2 c c of a 2 per cent solution of potassium iodide, and 2 c c of a 4 per cent solution of the same salt into the Torricellian vacuum of three barometer tubes mounted within a hot jacket The effect will be obvious from Fig 87

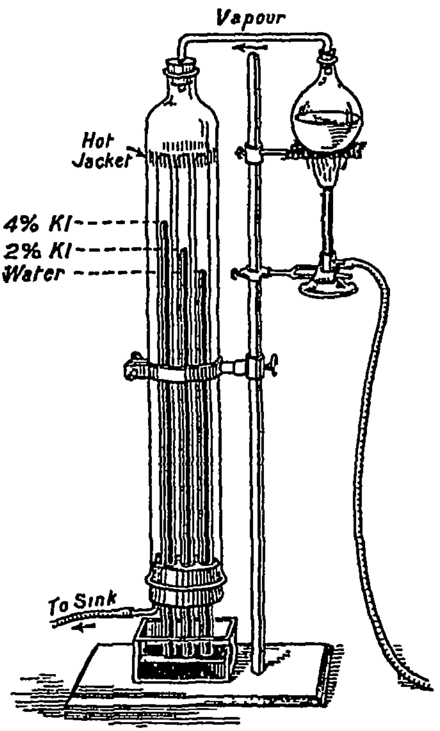

Fig 87 —The Vapour Pressure of Solutions

If w denotes the weight of substance in grams dissolved in 100 grams of solvent, and if p denotes the resultant lowering in the vapour pressure of the solvent, it can be shown by an extension of the above reasoning that the molecular weight of the solute is

$$\text{Molecular weight} = k\frac{w}{p}$$

where k is a constant whose numerical value depends upon the particular solvent used The method for determining the molecular weight of a substance from direct measurements of the lowering of the vapour pressure is of great theoretical interest but in practice the method is seldom employed

Deliquescence —If a soluble substance becomes moist by the condensation of moisture on its surface on exposure to the air the vapour pressure of the concentrated solution so formed is *less* than the vapour pressure of the moisture in the surrounding air Hence more moisture condenses on the surface, and this continues until the vapour pressure of the solution is equal to the vapour pressure of the aqueous vapour in the atmosphere Thus deliquescent substances not only become moist, but they attract so much moisture from the atmosphere that they dissolve in the water removed from the atmosphere, *e g* calcium chloride, potassium carbonate, sulphuric acid, etc

The evaporation of solutions —G F Fitzgerald (1896) has pointed out that the kinetic theory of evaporation describes the lowering of the vapour pressure of a solution in this manner The presence of non volatile molecules of the solute at the surface of the solution hinders the egress, but does not prevent, or possibly facilitates, the return of the volatile molecules (Fig 51) The gas analogy hypothesis of osmotic pressure assumes that the presence of a body in solution produces no effect or the same effect on the ingress or egress of the molecules of the solute, for the surface of a liquid with a non volatile solute is a perfect semipermeable membrane—water molecules can pass through the surface freely, but the molecules of the solute cannot It is a remarkable coincidence that with

dilute solutions the osmotic pressure is roughly the same as that which would be produced by the molecules of the solute if it were in the gaseous state, but, as previously indicated, the dynamical theory of the two must be intrinsically different

§ 6 Callendar's Vapour Pressure Hypothesis of Osmotic Pressure

The gas-analogy hypothesis of osmotic pressure—The "laws" associated with the names of Boyle, Charles, Dalton, and Graham, and the hypothesis of Avogadro, are but a few of the many striking analogies subsisting between the behaviour of gases confined in a given space, and substances in dilute solution We know enough about nature to believe that if two things are exactly alike, they will behave alike under the same circumstances, but when the things compared are not quite similar, we must be prepared for discrepancies. Analogy is not proof Had Isaac Newton measured the refractory power of native cadmium sulphide—greenockite—he would no doubt have said "greenockite is probably an unctous substance coagulated," and he would have been wrong As it happened, this prognostication turned out all right with the diamond The hypothesis that the osmotic pressure of a dilute solution is produced by the bombardment of the semipermeable membrane by the dissolved molecules gives a very plausible interpretation of the analogy between the behaviour of dissolved molecules, and the molecules of a gas brought out by J H van't Hoff, but the analogy appears to break down so completely with more concentrated solutions that a number of rival hypotheses have been advanced to explain the phenomena The principle of exhaustion, indicated on p 7, compels us to investigate other hypotheses H L Callendar's vapour pressure hypothesis (1909) is one of the most satisfactory, and it is superior, in many respects, to the gas-analogy hypothesis Callendar's hypothesis has been tested with somewhat concentrated solutions, and wherever data are available it has been eminently successful

The vapour pressure of a liquid under pressure—Experiment shows that the maximum vapour pressure of a solution can be altered in three ways (1) by altering the temperature (p 157), (2) by varying the concentration of the solution (Fig 87), and (3) by altering the pressure under which the liquid itself is confined The effect of pressure on the freezing point of water (*ON*, Fig 56) is an application of the third principle

The student might very properly raise the objection to the third method of altering the vapour pressure of a liquid, it has been shown, p 157, to be impossible to raise the pressure on a saturated vapour, without causing it to liquefy If a vertical cylinder, provided with a piston, contains nothing but water-liquid and vapour, it is quite true that the descent of the *piston will result in* the condensation of water vapour until all the vapour is liquefied, and as long as water vapour is present the vapour pressure remains constant On the contrary, if air as well as water vapour be present, it is easy to see that the volume of the air decreases, or *the pressure of the air on the surface of the liquid increases* during the descent of the piston The water vapour still supports its own share of the total pressure up to its maximum vapour pressure, and water vapour not quite so much as before will condense, consequently the liquid under a considerable external pressure can exert a greater vapour pressure than the maximum vapour pressure under atmospheric pressure

The relation between vapour pressure and osmotic pressure—It has been proved experimentally that the maximum vapour pressure of

a solution under very great pressures is rather greater than the maximum vapour pressure of the same solution under atmospheric pressures, see the curve *ON*, Fig 56 Again, the vapour pressure of a solution is *less* than the vapour pressure of the pure solvent, Fig 56 Consequently, if the pressure on a solution be sufficiently augmented, the pressure of its vapour can be made equal to the vapour pressure of the pure solvent under atmospheric pressure This is the condition necessary in order that solution and solvent can exist side by side in equilibrium If the vapour pressure of the solution were less than that of the pure solvent, the system would not be in equilibrium, because vapour would distil from the solvent into the solution until the vapour pressure of both were the same. Conversely, when a solution under its own osmotic pressure and the pure solvent are in equilibrium, it follows that their vapour pressures must be equal Hence, according to Callendar **The osmotic pressure of a solution represents the external pressure which must be applied in order to make its vapour pressure equal to that of the pure solvent** With this hypothesis Callendar has calculated the osmotic pressures of sugar solutions of different concentration from published vapour pressure data, and the results are in close agreement with observation

Concentration	180	300,	420	540	grams per litre
Observed osmotic pressure	14 6,	26 8	44 0	67 5	atmospheres
Calculated osmotic pressure	14 1,	26 8,	43 7,	67 6	atmospheres

Hence it is inferred that osmotic equilibrium depends upon the equality of the vapour pressure of the solution and of the pure solvent

A semipermeable membrane may be likened to a partition pierced by a large number of minute capillary tubes, suppose that the capillary tubes are not wetted by either the solvent or solution, then neither the liquid solvent nor the solution can enter the capillaries,[1] although vapour can diffuse through the capillary tubes But the vapour pressure of the solution on one side of one of the capillary tubes is less than the vapour pressure of the solvent on the other side, consequently, vapour will pass through the capillary and distil from the solvent to the solution Hence the volume of the solution will increase, and if the solution be confined in a closed vessel, the pressure must rise and continue rising until the vapour pressure of the solvent and solute are the same This increase in the pressure is the so called "osmotic pressure of the solution"

§ 7 The Relation between the Boiling Point of a Solution and the Molecular Weight of the Solute

In Figs 57 and 88 the curve *PO* represents the vapour pressure of the solid, and *OQ* the vapour pressure of the pure liquid The two curves intersect at the freezing point *O* Let *Q*, Fig 88, represent the boiling point of the solvent at 760 mm pressure, then since the vapour pressure of a solution is less than the vapour pressure of the pure solvent, let *O'Q'* represent the vapour pressure curve of a given solution Then *PM* will represent the freezing point of the solvent, and *PM'* the freezing point of the solution Since *PM'* is less than *PM*, the freezing point of the solution

[1] Unless the pressure on one of the liquids exceeds 100 atmospheres.

will be less than the freezing point of the solvent, and since PN' represents the boiling point of the solution and PN the boiling point of the solvent, the boiling point of the solution must be greater than the boiling point of the pure solvent. This agrees with experiment. For instance, with solutions of potassium iodide in 100 grams of water, G. T. Gerlach (1887) found

Boiling point	100°	101°	102°	103°	104°	105°
Potassium iodide	0,	15,	30,	45,	60,	74 grams

If the solutions are very strong the relation is not quite the same, but with dilute solutions, the raising of the boiling point of a dilute solution is directly proportional to the weight of the dissolved substance in a given weight of solvent. Double the concentration of the solution, and the elevation of the boiling point will be doubled. An equal number of molecules of the dissolved substance in the same quantity of a solvent give the same elevation of the boiling point—F. M. Raoult's law (1883–84). Hence the rise in the boiling point of a solvent is proportional to the number of molecules of the dissolved substance in solution, and inversely proportional to the molecular weight of the solute.

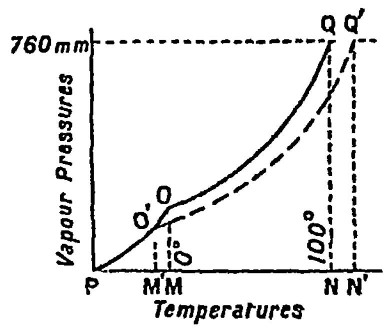

Fig. 88

One gram-molecule of cane sugar (342 grams) dissolved in 100 grams of water raises the boiling point of the water 5·2°, that is from 100° to 105·2°. This constant is called the boiling constant for water; it is sometimes called the "molecular elevation of the boiling point per 100 grams of solvent." Each solvent has its own specific boiling constant, e.g. acetone, 16·7; benzene, 26·7; ether, 21·6; carbon disulphide, 23·5; etc. The boiling constant is determined by finding the boiling point of, say, water and of aqueous solutions containing 0·02, 0·06, 0·10 gram-molecules of cane sugar, and calculating the results per 342 grams of cane sugar.

Suppose that w grams of a substance dissolved in 100 grams of water raised the boiling point of the water $b°$. Then, if M be used to denote the molecular weight of the substance, we have the proportion: $w : M = b : 5·2$, or, for substances dissolved in water,

$$\text{Molecular weight} = 5{\cdot}2\frac{w}{b} = K\frac{w}{t}$$

This enables the molecular weight of many substances to be determined from their effect on the boiling point of water. The particular solvent to be used depends on the solubility of the substance under investigation. If ether is used in place of water, 5·2 must be altered to 21·6, etc.

Examples.—(1) E. Beckmann (1890) found that 2·0579 grams of iodine dissolved in 30·14 grams of ether raised the boiling point of the ether 0·566°. What is the molecular weight of iodine? Here, 2·0579 grams of iodine in 30·14 grams of ether correspond with $100 \times 2{\cdot}0579 \div 30{\cdot}14 = w = 6{\cdot}8278$ grams of iodine in 100 grams of the solvent. Hence, $M = 21{\cdot}6 \times 6{\cdot}8278 \div 0{\cdot}566 = 254{\cdot}6$. This corresponds with the formula I_2 when iodine has a molecular weight of 253·84. The numbers seldom, if ever, coincide, but there can be no mistake in the significance of the figures.

(2) E Beckmann (1890) found that a solution of 1 4175 gram of phosphorus in 54 65 grams of carbon disulphide raised the boiling point 0 486° What is the molecular weight of the phosphorus? Answer Molecular weight, 120 16 The atomic weight of phosphorus is 31, hence the molecule of phosphorus is represented P_4

(3) A Helff (1893) found that 0 2096 gram of sulphur in 17 70 grams of carbon disulphide raised the boiling point 0 107° Hence show that the molecular weight of sulphur is probably S_8 Here $w = 1\ 17$, and the molecular weight is 259 This is close to the theoretical value 256 for S_8

E **Beckmann's process for the determination of boiling points (1888–96)**—The apparatus consists of a glass boiling tube *A*, Fig 89, with a piece of platinum wire sealed in the bottom, and packed with beads to prevent irregular boiling A side tube with a condenser *C* liquefies the vapour given off during the boiling, and the exposed end of the condenser is closed with a calcium chloride tube *D* The boiling tube is surrounded by a jacket of some non conducting material *E*, to prevent the radiation of heat The boiling tube is fitted with a Beckmann's thermometer, *T*, which can be read to $\frac{1}{100}$ of a degree, and set[1] so that the mercury is about half-way up the stem when the solvent is boiling The boiling tube has a stoppered side tube, *J*, for introducing the solution under investigation The whole is clamped to a stand and rests on an asbestos tray *F*

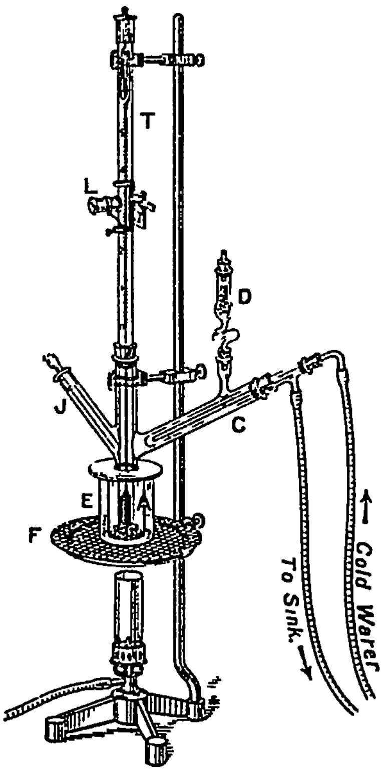

FIG 89—Beckmann's Apparatus for Boiling point Determinations

The boiling point of the solvent is first determined The boiling tube is weighed The solvent is introduced and its boiling point determined when the boiling is brisk and vigorous[2] A known weight of the substance is then introduced, and the boiling point of the solution determined A correction is made by subtracting 0 2 to 0 4 gram from the weight of the solvent in order to allow for the solvent condensed on to the walls of the apparatus and the condenser The actual correction depends upon the nature of the solvent and the particular form of the apparatus used The

[1] This thermometer has a reservoir of mercury at the top so that it can be set for use at any desired temperature as indicated in text books of laboratory processes In this way, an inconveniently long, or an inconveniently large number of thermometers are not needed The thermometer is always tapped before a reading to make sure the mercury is not lagging behind The lens *L* facilitates the reading of the thermometer

[2] The barometer should be read to make sure no appreciable change occurs during a determination

difficulty with this apparatus is to avoid fluctuations of temperature in the boiling tube due to the radiation of heat, dripping of the cold liquid from the condenser into the boiling solution, etc Many other forms of apparatus for this determination have been devised

Landsberger's method for the determination of boiling points (1898) — In W Landsberger's apparatus, a modification of which is shown in Fig 90, the solvent is boiled in the flask *A*, and the vapour passed into the solution *via* the tube *F* The temperature of the solution is raised to its boiling point by the latent heat of condensation of the vapour of the solvent The vapour of the solvent passes to the condenser *G* through *E* around the boiling tube, and thus the inner tube is jacketed with the vapour of the boiling solvent This reduces radiation losses The boiling point of the solvent is first determined, and a weighed amount of the solute is introduced into the inner tube *B*, which is graduated so that the boiling can be interrupted for a moment before more solute is added, and the volume of the solution read at a glance With the preceding notation, with water as a solvent,

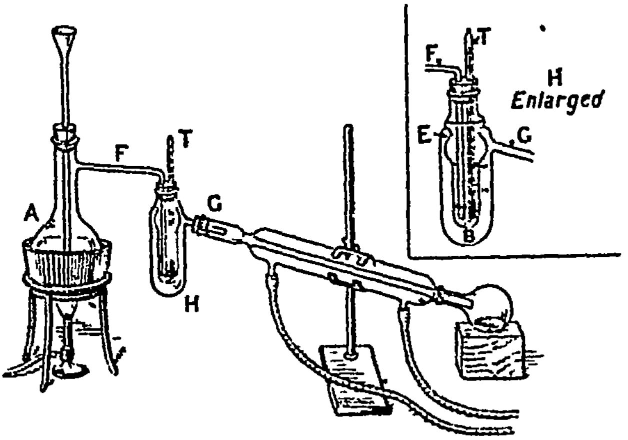

Fig 90 —Landsberger's Apparatus for Boiling-point Determinations

$$\text{Molecular weight} = 5\ 2\frac{w}{b}$$

where w denotes the weight of the substance per 100 c c of the solvent, and b represents the elevation of the boiling point If other solvents be used 5 2 is altered thus for acetone, 22 2, benzene, 32 8, ether, 30 3, carbon disulphide, 26 If the boiling tube be weighed so that the amount of solvent is determined by weight, and not by volume, the original formula, on p 215, is used

EXAMPLE —If 0 820 gram of a substance with 8 1 c c of acetone gave a rise of 1 47° in the boiling point of the solvent, what is the molecular weight of the substance? Here, $w = 100 \times 0\ 820 \div 8\ 1 = 10\ 24$ In the above formula, 5 2 for water is changed to 22 2 for acetone Hence the desired molecular weight is $22\ 2 \times 10\ 24 \div 1\ 47 = 154$

In the laboratory, advantage is taken of the fact that the boiling point of a solution is higher than the boiling point of the pure solvent to get liquids for baths, etc, boiling a few degrees higher than water, by dissolving the necessary amount of a salt in water For example, a saturated solution of sodium nitrate boils at 120°, and a saturated solution of sodium chloride at 180°

§ 8 The Relation between the Freezing Point of a Solution and the Molecular Weight of the Solute

with nec say changes

Similar remarks apply *mutatis mutandis* to the freezing point of solutions as were made with reference to the boiling point A study of Fig 88 will show that if the vapour pressure of a solution is less than that of the pure solvent, the vapour pressure curve will cut the ice curve at a temperature below the freezing point of the pure solvent This means that the freezing point of a given solution will be lower than the freezing point of the pure solvent, and experiment shows that the lowering of the freezing point will be proportional to the weight of the substance dissolved in a given weight of the solvent This reminds us of Blagden's law, p 161 **The depression in the freezing point is proportional to the weight of the dissolved substance in a given weight of the solvent, and inversely proportional to the molecular weight of the dissolved substance**

Equal gram molecules of different substances in the same solvent depress the freezing point to the same extent—F M Raoult's law (1883–84) A solution of sugar (342 grams), methyl alcohol (32 03 grams), etc, in 100 grams of water depress the freezing point 18 5° This is the freezing constant for water It is also called "the molecular depression of the freezing point per 100 grams of solvent" Each solvent has its own specific freezing constant, *e g* acetic acid, 38 88°, benzene, 49°, mercury, 425°, naphthalene, 69°, etc

If w grams of a substance, molecular weight M, dissolved in 100 grams of solvent, lowers the freezing point $f°$, we have the proportion $w : M = f : 18\ 5$ for water, or, for substances dissolved in water,

$$\text{Molecular weight} = 18\ 5\frac{w}{f}$$

This enables the molecular weight of a substance to be computed from its effect on the freezing point of water The particular solvent to be selected is of course determined by the solubility of the substance under investigation, and the number 18 5 must be replaced by another if a different solvent be used

EXAMPLES —(1) W Tammann (1889) found that a solution of 0 022 gram of sodium in 100 grams of mercury lowered the freezing point of mercury 0 39° What is the molecular weight of sodium? Here, $M = 425 \times 0\ 022 \div 0\ 39 = 23\ 8$ Hence the atomic and molecular weights are the same

(2) W R Orndorff and J White (1893) found that a solution of 0 2735 gram of hydrogen peroxide in 19 86 grams of water lowered the freezing point of water 0 746° What is the molecular weight of hydrogen peroxide? Here $w = 100 \times 0\ 2735 \div 19\ 86 = 1\ 3773$ $f = 0\ 746$, hence, $M = 34\ 2$ This corresponds with the molecule H_2O_2 An earlier determination by W Tammann (1889) gave H_4O_4, but this was afterwards found to be due to the use of an impure sample

(3) J Hertz (1890) found that 2 423 grams of sulphur in 100 grams of naphthalene lowered the freezing point of naphthalene 0 641° hence show that the molecular weight of sulphur under these conditions corresponds with the formula S_8 Answer: The molecular weight by experiment is 262, and by calculation for S_8, 256

E Beckmann's process for the determination of freezing points—Freezing-point determinations are usually made in Beckmann's apparatus.

The tube *A*, Fig 91 with a side neck, *B*, is weighed, and about 15 c c of the solvent are added and the tube is weighed again The Beckmann's thermometer, reading to the $\frac{1}{100}$ of a degree and set so that the mercury is near the top of the scale when set for the freezing point of the solvent, has a reading lens The thermometer *T* and a stirrer *S* are placed in the solvent, and the whole arrangement is placed in a glass tube *A* which serves as an air jacket This is surrounded by a vessel *D* of water or some liquid at a temperature about 5° below the freezing point of the solvent This vessel is fitted with a thermometer T_1 and stirrer S_1 The temperature recorded by the thermometer slowly falls until the solvent begins to freeze, it usually falls from 0 2° to 0 3° below the freezing point of the solvent, and then begins to rise to the freezing point proper The thermometer should always be tapped before a reading is taken to make sure the mercury is not lagging behind The highest point reached by the mercury in the thermometer is taken to be the freezing point of the solvent Owing to undercooling, it is sometimes difficult to start the freezing of the solution In that case, a few pieces of platinum foil, or a minute fragment of the frozen solvent, will start the freezing It is sometimes necessary to introduce a correction for undercooling as indicated in text-books for the laboratory Each determination should be repeated two or three times and the successive observations should agree within 0 002° to 0·003° When the freezing point of the solvent has been determined, add a sufficient amount of the substance under investigation to give a depression of 0 3° to 0 5°. After the freezing point has been determined again, find the freezing point after adding a second and then a third portion of the substance under investigation

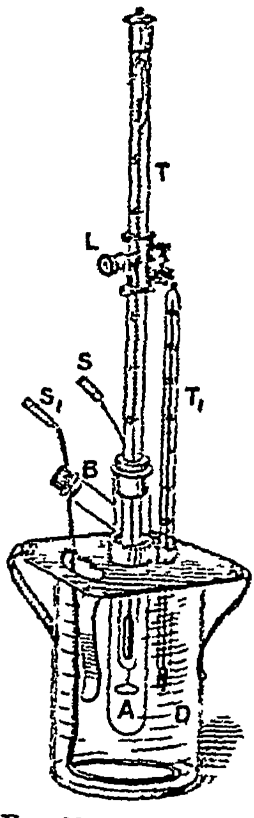

FIG 91 —Beckmann's Apparatus for Freezing-point Determinations

The molecular weights of substances relative to the weights of the hydrogen molecule have been determined from the vapour density determinations and Avogadro's hypothesis The osmotic pressure and related properties of solution enable the molecular weights of liquids and solids in solution to be determined. There is an extensive choice of solvents, and it is possible to utilize such widely different solvents as stearic acid, mercury, ether, fused metals, etc Molten salts containing water of crystallization have been used—*e g* sodium sulphate, Na_2SO_4 $10H_2O$; calcium chloride, $CaCl_2$ $6H_2O$, lithium nitrate, $LiNO_3$, sodium chromate, Na_2CrO_4 $10H_2O$, etc —and the results are similar to those obtained with water as a solvent

The molecular weights of a great many substances in solution are in agreement with those furnished by the vapour density *method*, yet there are some irregularities The molecular weights of substances in solutions are sometimes greater and sometimes less than what we should expect The results are then said to be abnormal.

§ 9 Anomalous or Abnormal Results for the Molecular Weights of Substances in Solution

When a fact appears to be opposed to a whole train of deductions it invariably proves to be capable of bearing some other interpretation —SHERLOCK HOLMES

The meaning of "abnormal" in science —We sometimes say that a phenomenon "ought to take place," but it does not We have just used the words "abnormal" and "anomalous" These terms are not very happily chosen, and, as indicated on p 82, they are sometimes used rather carelessly The terms are not intended to imply that nature is erratic, arbitrary, and lawless The words simply mean that in groping for the truth, an unexpected result has been obtained, which once stood, or now stands, challenging investigators to show how the unexpected should have been expected. Some of the most treasured generalizations in science have been won by investigating the "abnormal"

Revision of the gas equation pv = RT —Let us return to the gas equation,

$$\frac{pv}{T} = \frac{p_1v_1}{T_1}$$

Remembering that the density D of a gas is equal to the molecular weight M divided by the volume v, or, $M = Dv$, we get $p/TD = p_1/T_1D_1$ when $M = M_1$ Let M, D, and v respectively denote the molecular weight, density and volume of the gas in one condition of temperature and pressure, and M_1, D_1, and v_1, the same constants for another condition of temperature and pressure, we obtain, by substitution in the preceding equation $pv/MT = p_1v_1/M_1T_1$ If we take the volume v_1 at some standard temperature T_1 and pressure p_1, the numbers p_1, v_1, and T_1 will always have one fixed value Let R denote this constant value of p_1v_1/T_1 The gas equation then assumes the form

$$pv = \frac{M}{M_1}RT\text{, or, } pv = nRT$$

where n stands in place of the ratio of the molecular weights of the gas in the two conditions, M/M_1 If the molecules of the gas neither dissociate nor polymerize when the conditions change, $M = M_1$, or $pv = RT$ because $n = 1$ But if the gas molecules polymerize or condense so that, say, two molecules combine together to form one molecule, there will be only half as many molecules in a given space as before, $M = \frac{1}{2}M_1$, and $pv = \frac{1}{2}RT$ If, however, the gas dissociates or decomposes so that each molecule of the gas forms two molecules of another gas or gases, then $M = 2M_1$, and we have $pv = 2RT$ Hence the ordinary gas equation **pv = RT, is a special case of the more general relation pv = nRT, where the numerical value of n indicates whether or not the gas keeps the same molecular concentration during the change If n = 1, there is neither dissociation nor polymerization, if n be less than unity, the gas polymerizes, and if n be greater than unity, the gas dissociates when the conditions are changed**

If the molecules of a dissolved substance are the same as the molecules would be if the substance were in the gaseous condition, the relation between the pressure, temperature, and concentration will be represented

by the expression, $pv = nRT$, or, since the concentration c is inversely as the volume, by

$$\frac{p}{c} = nRT$$

As before, if n be unity, the molecules of the substance in solution and in the gaseous condition are presumably similar, if n be greater than unity, the molecules dissociate when they pass into solution, and if n be less than unity, the molecules polymerize If we apply the uncorrected relation, $p/c = RT$, it is now easy to see that if n be greater than unity (dissociation), the osmotic pressure will appear too high, and if n be less than unity (polymerization), the osmotic pressure will appear too low When we speak of the lowering of the osmotic pressure, we also imply that the vapour pressure is increased, the boiling point is lowered, and the freezing point raised, and conversely, the raising of the osmotic pressure implies that the boiling point is raised, and the vapour pressure and freezing point are lowered

Abnormally low osmotic pressures—polymerization —The depression of the freezing point of a solution of alcohol in benzene is just about half what we should expect if the molecules of alcohol were represented by the regular formula C_2H_5OH This means that the molecules of alcohol—C_2H_5OH—in benzene solutions are doubled, and the molecule of alcohol is accordingly $C_4H_{10}(OH)_2$ in benzene solution This phenomenon is common with molecules possessing hydroxyl, *i e* OH groups Formic —H CO OH—and acetic—CH_3 CO OH—acids, and indeed water, behave in a similar manner, and we know that if these acids be vaporized, they appear to have twice the molecular weight of what would obtain if their molecules could be really represented by the ordinary formulæ Otherwise expressed, the molecules are polymerized It is also necessary to remember that if the dissolved substance freezes out along with the solvent so as to form a kind of solid solution, the freezing point of the solution will be lower than that calculated from the regular molecular formula of the dissolved substance Sometimes, indeed, the freezing point actually rises There are many examples—solutions of lead, cadmium, tin, and gold in mercury, antimony in tin, etc

Abnormally high osmotic pressures—dissociation —A very considerable number of aqueous solutions of acids, bases, and salts furnish a much greater osmotic pressure than we should naturally expect The deviation of a gas from Avogadro's law is usually explained by assuming that the molecules of the gas are dissociated into simpler forms Iodine molecules, I_2, at high temperatures appear to behave as symbolized $I_2 = I + I$ S Arrhenius (1887) sought to explain the deviations of the molecular weights of salts, acids, and bases in aqueous solutions by assuming that the molecules are dissociated into simpler parts The molecules of sodium chloride, for instance, are supposed to be dissociated in aqueous solutions into two parts—Na and Cl The idea came as a surprise, and much opposition has been raised against this interpretation of the results, because there are no signs of chemical action which might be expected if the molecule of sodium chloride were dissociated into Na and Cl on solution in water Accordingly, other hypotheses have been invented to make the first hypothesis fit the facts In spite of this, Arrhenius' hypotheses at once explains in a seductive and plausible manner the abnormally high osmotic

pressures obtained for these substances. There is a strange coincidence. Arrhenius determined the value of n—the number of molecules in the above equations for ninety different substances. He noticed at once that these substances could be roughly divided into two classes: those which gave values of n nearly unity were either non-conductors or poor conductors of electricity; whereas those which gave values of n materially greater than unity were fair or good conductors of electricity. In the following table n may be taken to represent, within the limits of experimental error, the relative number of molecules formed when one molecule of the substance is dissolved.

TABLE VIII.—NORMAL AND ABNORMAL OSMOTIC PRESSURES.

Non-conductors		Conductors	
Substances in solution	n	Substances in solution	n
Methyl alcohol	0.94	Calcium nitrate	2.48
Mannite	0.97	Magnesium sulphate	1.25
Cane sugar	1.00	Strontium chloride	2.69
Ethyl acetate	0.96	Potassium chloride	1.81
Acetamide	0.96	Lithium chloride	1.92

We naturally inquire: What connection, if any, subsists between the alleged dissociation of the molecules of a substance in a solution and the conduction of electricity? How can one molecule of sodium chloride, one molecule of lithium chloride, and of hydrogen chloride, each furnish what appears to be two molecules when dissolved in water?

Questions

1. An aqueous solution of LiCl containing 8.5 grams in 1000 c.c., boils at 101.97° C. (760 mm.). What is the percentage dissociation of the LiCl? (Atomic weights: Li = 7, Cl = 35.5. Molecular raising of boiling point of water = 0.52° C.)—*Worcester Polytechnic Inst., U.S.A.*

2. 7.20 grams of a substance dissolved in 100 grams of water gave rise to an osmotic pressure of 9.65 atmospheres at 22°. Calculate the molecular weight of the substance.—*Sheffield Univ.*

3. A solution of 6.3 grams of a non-electrolyte in water, total volume 1000 c.c., freezes at −0.279° C. What is the molecular weight of the substance in solution? (Molecular lowering of the freezing point of water = 18.6.)—*Worcester Polytechnic Inst., U.S.A.*

4. What is meant by the term osmosis? Describe exactly what happens when a vessel with a semipermeable wall containing a solution of such a substance as sugar is placed in pure water. What is (*a*) the effect of increasing the strength of the sugar solution, and (*b*) the effect of raising the temperature of the whole apparatus?—*Univ. North Wales.*

5. What do you understand by the expressions "additive," "constitutive,"[1] and "colligative"? Illustrate your answer by examples.—*St. Andrews Univ.*

6. How have the freezing points of dilute solutions been exactly observed? What is the bearing of these observations on chemical theory?—*New Zealand Univ.*

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[1] CONSTITUTIVE PROPERTIES have not yet been discussed. In these the preponderating factor is the mode of grouping of the atoms within the molecule. Examples will be indicated later—see "Isomerism."

7 The freezing point of an aqueous solution is $-1.5°$ C Find the relative lowering of the vapour pressure of the solution (The molecular depression for water is 18 70)—*St Andrews Univ*

8 Describe some experiment showing the phenomenon of "osmotic pressure" By what means has a relation been observed between the molecular weight of certain soluble substances and the osmotic pressure which they are supposed to exert? If the lower part of a U-tube be filled with a solution of sugar, and then pure water be gently poured into one limb so that the upper surface in one limb is pure water, and in the other limb is a solution of sugar, is osmotic pressure exerted, and if not, why not?—*New Zealand Univ*

9 What do you understand by the term "osmotic pressure"? Describe in outline any two processes, one direct, the other indirect, for measuring osmotic pressure Explain carefully how the molecular weight of a substance in solution can be determined when the osmotic pressure which it sets up is known —*Board of Educ*

10 What is osmotic pressure? Has this any connection with the pressure of a gas? Alcohol is said to be normal in regard to its vapour pressure and its osmotic pressure, ammonium chloride has an abnormal vapour pressure and osmotic pressure Explain the meaning of the terms normal and abnormal used here —*Sydney Univ*

11 Explain how it is that vegetables will cook faster when boiled in a concentrated solution of salt than when boiled in water alone

12 Describe the effects produced by soluble and insoluble substances on the boiling and melting points of water What explanation of the differences observed when common salt and sugar are respectively dissolved in sufficient pure water to form dilute solutions of the same molecular concentration? To what other properties of solutions does this explanation apply?—*Panjab Univ*

13 Explain the principle of Raoult's method of determining molecular weights by observation of the freezing point Give some account of its applications, and the chief results obtained —*London Univ*

CHAPTER XIII

Chlorine and Hydrogen Chloride

§ 1 The Stassfurt Salt Beds

The remarkable deposits of potassium, magnesium and sodium salts in the country around Stassfurt, in Prussian Saxony, may be very roughly divided into four strata, illustrated diagrammatically in Fig 92

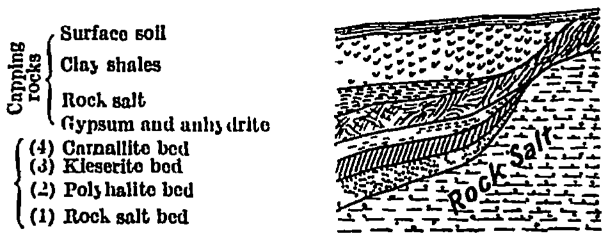


Fig 92 —Diagrammatic Geological Section of a Part of the Stassfurt Salt Bed

(1) *Rock salt bed* —An immense basal bed of rock salt, broken up at fairly regular intervals with 2 to 5 inch bands of *anhydrite*—$CaSO_4$

(2) *Polyhalite bed* —Above the basal salt is a layer of rock salt, sometimes 200 feet thick, mixed with bands of magnesium chloride and *polyhalite*—$2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$

(3) *Kieserite bed* —Resting on the polyhalite bed is a layer of rock salt, sometimes 100 feet thick, mixed with layers of *kieserite*—$MgSO_4 \cdot H_2O$—and other sulphates, about 1 foot thickness

(4) *Carnallite bed* —Finally comes a reddish layer of rock salt associated with masses of *kainite*—$K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$, *carnallite*—$KCl \cdot MgCl_2 \cdot 6H_2O$, and a few other salts of magnesium and potassium, *e.g* , *sylvine*—KCl and *leonite*—$MgSO_4 \cdot K_2SO_4 \cdot 4H_2O$

These deposits are capped by layers of gypsum—$CaSO_4 \cdot 2H_2O$—and anhydrite—$CaSO_4$, rock salt , bunter clay shales , and finally the surface soil In addition to gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), and rock salt ($NaCl$), the principal salts found in the Stassfurt deposits are

Sylvine	KCl
Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$
Kieserite	$MgSO_4 \cdot H_2O$
Schönite	$MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$
Kainite	$MgSO_4 \cdot K_2SO_4 \cdot MgCl_2 \cdot 6H_2O$
Polyhalite	$MgSO_4 \cdot K_2SO_4 \cdot 2CaSO_4 \cdot 2H_2O$

With several other salts of lesser importance, e.g., *astrakanite* ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$), *boracite* ($2Mg_3B_8O_{15} \cdot MgCl_2$), *glauberite* ($Na_2SO_4 \cdot CaSO_4$); *leonite* ($MgSO_4 \cdot K_2SO_4 \cdot 4H_2O$), etc.

History.—In the thirteenth century salt springs—called "sool"—were well known in the region of Stassfurt, and a certain amount of salt—sodium chloride—was obtained from them, but the springs were abandoned when rock salt was discovered in other parts of Germany. About 1840, borings were made in the hope of finding deposits which would give a good quality of salt, and about 1850, shafts were sunk, and rock salt mined. The material excavated with the rock salt was rejected as worthless, and called Abraumsalze—German *Abraum*, refuse; *Salze*, salts. As a result of the investigations of Rose and Rammelsberg, the Abraumsalze were recognised to be a valuable source of potassium and magnesium. Processes were then devised for the extraction of the potassium and magnesium salts with the result that the rock salt became of little value, and the Abraumsalze became of primary importance. A. Frank erected the first works for the extraction of potassium chloride in 1861, and an important industry, controlled by the "German Kali Syndicate," has been established. The Stassfurt salt deposits have been the subject of elaborate investigations by J. H. van't Hoff and his pupils in the light of the phase rule of J. W. Gibbs.

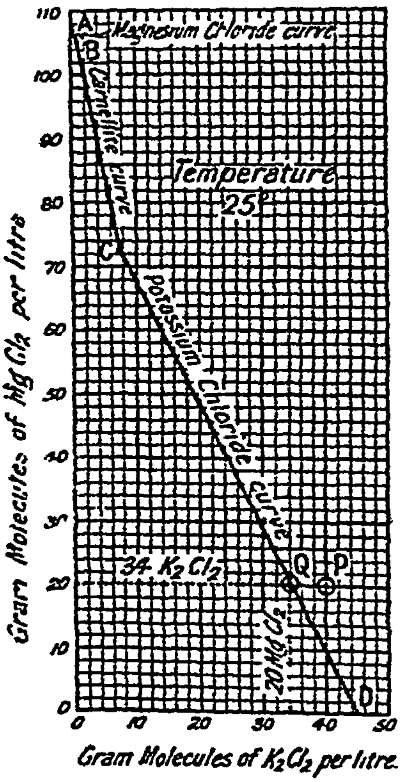


Fig. 93.—Solubilities of Magnesium and Potassium Chlorides in Mixed Solutions.

Crystallization of salts from mixed solutions.—The simple cases of the crystallization of a solution saturated with but one salt was discussed on p. 23, and of solutions of two salts which do not react with one another, nor form hydrates, was discussed on p. 170. The phenomenon is more complex when the salts present in the solution form a series of hydrates, or when the salts can react with one another to form double salts. A solution of potassium chloride and magnesium chloride not only furnishes crystals of magnesium chloride, $MgCl_2 \cdot 6H_2O$, and of potassium chloride, KCl, but also crystals of the double salt, $KCl \cdot MgCl_2 \cdot 6H_2O$—carnallite. Referring to Fig. 93, the line *AB* represents the effect of additions of potassium chloride on the amount of magnesium chloride required to form a saturated solution at 25°. The solubilities are here expressed in terms of gram-molecules of $MgCl_2$ and of K_2Cl_2 per 1000 c.c.[1] The line *BC*

[1] "K_2Cl_2" is written in place of "2KCl" without any implication that the molecule of potassium chloride is K_2Cl_2. This is done to keep equivalent molecules of magnesium and potassium chlorides as units for ordinates and abscissæ.

represents the amount of carnallite in a saturated solution as the amount of potassium chloride is increased, and the line *CD* represents the amount of potassium chloride in a saturated solution as the amount of magnesium chloride is increased.

All solutions represented by points on the lines *ABCD* are saturated with one of these salts If therefore we start with a solution containing, say, 20 gram-molecules of magnesium chloride, and 40 gram molecules of K_2Cl_2 per litre, the composition of the solution will be represented by a point *P* on the diagram Crystals of potassium chloride will be deposited until the composition of the solution is represented by a point *Q* on the line *CD*, that is, potassium chloride will be deposited until the solution contains 20 gram molecules of magnesium chloride, and 34 of K_2Cl_2 per litre If the solution be concentrated by evaporation at 25°, potassium chloride will continue separating until the composition of the solution can be represented by a point *C*, that is, until the solution contains about $5\frac{1}{2}$ gram-molecules of K_2Cl_2, and $72\frac{1}{2}$ gram-molecules of $MgCl_2$ per litre If the mother liquid be still further concentrated at 25°, crystals of carnallite and of potassium chloride will separate until the concentration of the solution is represented by a point *B*, corresponding with one gram molecule of K_2Cl_2, and 105 gram molecules of $MgCl_2$ Any further concentration of the mother liquid will lead to the separation of magnesium chloride and carnallite in constant proportions until the solution is dry

If the temperature at which the crystals are removed be different, different results will be obtained, because of differences in the solubilities of the different salts at varying temperatures, the formation of hydrates at temperatures above or below transition points, etc The same principles obtain even with still more complicated examples, say a mixture of potassium chloride and magnesium sulphate, where we have the reaction, $2KCl + MgSO_4 = MgCl_2 + K_2SO_4$ This solution may lead to the separation of crystals of potassium chloride and sulphate, magnesium chloride, two hydrates ("$6H_2O$" and "$7H_2O$") of magnesium sulphate, carnallite, and schönite—$K_2SO_4.MgSO_4.6H_2O$

Origin—It is generally thought that the Stassfurt beds are of marine origin, and have been formed by the natural evaporation of water, during countless years, in an inland prehistoric sea The sea must have been periodically replenished by water bringing in more salts The order in which salts are deposited from the evaporation of sea-water is very nearly the same as the geological succession observed at Stassfurt Neglecting the calcium sulphate, the evaporation of sea water furnishes successively (1) a deposit of sodium chloride, (2) sodium chloride mixed with magnesium sulphate, (3) sodium chloride and leonite, (4) sodium chloride, leonite, and potassium chloride, or sodium chloride and kainite, (5) sodium chloride, kieserite, and carnallite, (6) sodium chloride, kieserite, carnallite, magnesium chloride, and (7) the solution dries without further change

Uses—The Stassfurt salts furnish magnesium salts which are used for the preparation of magnesium and its salts The potash salts are largely used as manures in agriculture, and the potassium chloride is used as a basis for the manufacture of the many different kinds of potassium salts used in commerce—carbonate hydroxide, nitrate, chlorate, chromates, alums, ferrocyanide, cyanide, iodide, bromide, etc. Chlorine and bromine

are obtained from the mother liquids by electrolytic and other processes. Boric acid and borax are prepared from boracite. Cæsium and rubidium are recovered from crude carnallite and sylvine

§ 2 Sodium and Potassium Chlorides

Sodium chloride commonly called "salt," is considered to be an essential constituent of animal food One writer estimates that about 29 lbs. of salt per head of population per annum is used directly or indirectly with the food for man The 0·1 per cent of hydrochloric acid present in the gastric and mucous fluids of the alimentary canal is derived from the decomposition of the salt taken in with the food Plant-eating animals get the salt they require from grass and leaves, herbivorous animals have been known to travel hundreds of miles to a "salt-lick" ("salt spring") in order to satisfy their craving for salt Carnivorous animals get their salt from the blood of the animals on which they feed

The occurrence of salt—Rock salt occurs in transparent or translucent cubic crystals, either colourless or varying in tint from white, to dirty grey, to yellow, to reddish yellow, and sometimes blue or purple. It is sometimes called *halite* Rock salt is found in Nantwich, Northwich, Middlewich (Cheshire), Droitwich[1] (Worcestershire), Stassfurt (Prussian Saxony), Cardona, Castile (Spain), California Utah, Kansas, New York, Virginia, Ohio, Michigan (United States), and numerous other places. The mines at Wielicza (Galicia Austria) have been worked continuously for 600 years The salt deposit is said to be 500 miles long, 20 miles broad and 1200 feet thick. The galleries and chambers in this mine extend over 30 miles in length and yield 55,000 tons per annum A comparatively large amount of salt is dissolved in sea water, and in the water of many salt springs, and salt wells The water of the Mediterranean Sea, for instance, contains 3·37 per cent of solids in solution On evaporation to dryness, the residue contains 77·0 per cent of sodium chloride, 2·5 of potassium chloride, 8·8, magnesium chloride, 2·8, calcium sulphate, 8·3, magnesium sulphate, 0·1, magnesium and calcium carbonates, and 0·5 per cent of a mixture of sodium and magnesium bromides

The separation of salt from sea-water—Countries not supplied with rock salt must either import salt from more favoured countries, or resort to the concentration of sea-water, or the water of salt springs Evaporation is not an expensive process in warm countries, or where coal is cheap, *e g* on the shores of the Mediterranean Sea the sea-water is concentrated by evaporation in large shallow tanks—"salterns"—exposed to wind and sun As the solution—"brine"—becomes concentrated, the crystals of salt which separate are lifted out by means of perforated shovels, and allowed to drain beside the evaporation tanks The mother liquid—"bittern"—was once used for the manufacture of bromine. In cold countries, *e g* on the shores of the White Sea (Russia), the sea-water is concentrated by freezing (p 161) Ice first separates, and the residual brine is further concentrated by evaporation over a fire

The purification of rock salt—Rock salt is often mined by bringing

[1] The names of these localities indicate the antiquity of the salt industry, since, in Saxon times, a place where salt was dug was called a "wich"

the solid salt to the surface in lumps In some salt beds, the salt is mined by forcing water into the beds *via* a well made for the purpose The brine is afterwards pumped to the surface, and the liquid concentrated in salterns, or by allowing the solution to trickle from elevated tanks over ricks of brushwood—"graduators"—so arranged that the solution is fully exposed to the prevailing winds The liquid may be afterwards concentrated by evaporation in shallow pans heated artificially, particularly if fuel is cheap As the salt crystallizes out, it is removed by means of perforated shovels If much calcium sulphate be present, it will separate first It must therefore be removed before the salt The potassium and magnesium salts separate last If fine-grained "table salt" is needed, the brine is evaporated rapidly near its boiling point, but for the manufacture of coarse grained "fish salt" the evaporation is conducted slowly at a comparatively low temperature (45°) so as to get the salt in comparatively large crystals The salt obtained by the evaporation of sea water will be contaminated with small quantities of other salts as impurities calcium chloride, magnesium chloride, calcium sulphate, and magnesium sulphate Cheshire salt, for instance, contains about 98 3 per cent of sodium chloride, the remaining impurities are mainly insoluble matter, calcium sulphate, and magnesium and calcium chlorides

The extraction of potassium chloride from carnallite—Potassium chloride occurs as sylvine—KCl—in the Stassfurt deposits, and associated with magnesium chloride in carnallite Potassium chloride was formerly obtained from sea water, but much of the potassium chloride of commerce is now made from carnallite—$KCl.MgCl_2.6H_2O$—of the Stassfurt deposits The crude carnallite contains about 61 per cent of carnallite, 25 per cent. of kieserite, 12 per cent of rock salt, and 2 per cent of anhydrite and clay This salt is crushed and digested in large tanks with the mother liquid left from preceding operations. This liquid contains chiefly magnesium chloride The mixture is heated by blowing steam into the liquid. The potassium chloride readily dissolves in this liquid, while most of the sodium chloride and magnesium sulphate, associated with the crude carnallite, remain as an insoluble residue The liquid is allowed to settle for an hour, and then decanted into large iron vats, where crystals containing 64 to 69 per cent of potassium chloride are deposited The impurities are mainly sodium chloride (20–22 per cent), magnesium chloride (7 5–8 5 per cent), and 0 4 per cent of magnesium bromide and calcium sulphate The principle underlying the process will appear from the study of Fig 93 The crystals of potassium chloride so obtained are washed in cold water so as to remove the more soluble sodium chloride This process yields a product containing 84 to 98 per cent of potassium chloride, according to the number of washings The further purification of the salt involves a re solution and re crystallization The mother liquors are washed up for more salts, and finally used for the extraction of a fresh lot of crude carnallite

The purification of sodium and potassium chlorides—Sodium as well as potassium chloride can be purified by adding concentrated hydrochloric acid to a cold concentrated aqueous solution of the respective salts, better results are obtained by passing gaseous hydrogen chloride through the salt solutions The impurities remain in solution while the chlorides are precipitated in a very fair state of purity.

Properties.—Both chlorides crystallize in cubes, and the two salts are isomorphous The crystals are anhydrous. A little water may be mechanically entangled with the crystals, which causes the salts to decrepitate when heated. Sodium chloride melts at 801°, and potassium chloride is said to melt at about 790°. Both salts sublime at higher temperatures without decomposition. Sodium chloride boils at about 1750° The solubilities of the two salts in water were discussed on pp 159 and 171. A comparison of the related chlorides of lithium sodium, potassium, rubidium, and cæsium, shows that they all crystallize in cubes when anhydrous—Fig. 61, left Their solubilities, expressed in grams per 100 c c of water at 15° are:

Lithium	Sodium	Potassium	Rubidium	Cæsium
80	36	33 4	80	very high

and the solubilities in alcohol follow the same rule, sodium and potassium chlorides being almost insoluble in alcohol

Composition.—The composition of both salts has been established in the same manner By analysis, J. S Stas found sodium chloride contained 39 39 per cent of sodium, and 60 61 per cent. of chlorine Hence after division by the respective atomic weights of these elements, we get the atomic ratio Na Cl = 1 : 1 corresponding with the formula $(NaCl)_n$. W. Nernst (1903) found the vapour densities of both sodium and potassium chlorides at 2000° corresponded respectively with the formulæ NaCl and KCl

Uses of sodium chloride—Salt is used for seasoning food—table salt Salt for table use should be free from magnesium and calcium chlorides, for these substances make salt very deliquescent—particularly in moist weather Salt is also used for preserving meat, fish, etc., in the manufacture of sodium salts, soaps etc ; in glazing common pottery—drain pipes some sanitary goods, etc—" salt glaze" ; and also in the manufacture of chlorine compounds, directly or indirectly.

§ 3 Hydrogen Chloride—Preparation and Properties.

Molecular weight, HCl = 36 47, melting point −112 5°, boiling point, between −83° and −84 , critical temperature −52 3° Vapour density (H_2 = 2), 36 49, (air = 1) 1 269 One litre weighs 1 641 grams under normal conditions Specific gravity of liquid, 0 908 at 0°

Preparation—When sodium or potassium chloride is treated with warm dilute sulphuric acid (1 : 1) in a flask (Fig. 94), a gas is given off. The gas is very soluble in water and it cannot be collected over water, but it can be collected over mercury. In general laboratory work, it is often convenient to collect relatively heavy gases by the upward displacement of air. The gas was once called the "spirit of salt," but is now called "hydrogen chloride" and symbolized "HCl" The reaction is represented: $H_2SO_4 + NaCl = NaHSO_4 + HCl$. The gas can be dried by passage through wash-bottles containing concentrated sulphuric acid If the concentrated acid be employed with an excess of sodium chloride, at a rather more elevated temperature, the reaction is represented by: $H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl$ The same gas is often made in the laboratory at ordinary temperatures by mixing concentrated hydrochloric acid

with an excess of sodium or ammonium chloride and dropping concentrated sulphuric acid from a tap funnel into the mixture, as indicated in Fig 47

Properties —Hydrogen chloride is a colourless gas which irritates the mucous membrane when inhaled It forms dense fumes in moist air The gas is incombustible, and a non-supporter of combustion Hydrogen chloride is extremely soluble in water 1 c c of water at 0° dissolves 525 c c of the gas, and at 20°, 440 c.c The heat of solution is $HCl + Aq = HClaq + 17\ 4$ Cals. The aqueous solution is strongly acid, and is called "hydrochloric acid," "spirits of salt," or "muriatic acid"—from the Latin *muria*, brine Hydrogen chloride partially dissociates into free chlorine and hydrogen at about 1500° $2HCl \rightleftharpoons H_2 + Cl_2$. Hydrogen chloride is easily condensed to a colourless liquid by pressure At 10° a pressure of 40 atmospheres will liquefy the gas, and at —16°, 20 atmospheres suffice The liquid boils at —83 7° under ordinary atmospheric pressures The liquid freezes to a white crystalline mass melting at —112 5° The liquid does not act on many metals which are vigorously attacked by

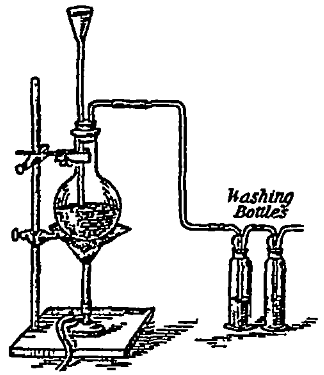


FIG 94 —Preparation of Hydrogen Chloride

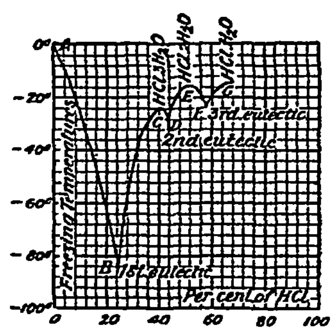


FIG 95 —Freezing point Curves of Mixtures of Hydrogen Chloride and Water

the aqueous solution of hydrogen chloride Neither the dry liquid nor the dry gas acts on blue litmus.

The freezing temperatures of aqueous solutions of hydrogen chloride.—The freezing temperatures of aqueous solutions of hydrogen chloride of different concentrations have been determined for solutions containing less than 67 per cent of hydrogen chloride, as shown in Fig 95 —F F Rupert (1909) Starting with pure water, the addition of hydrogen chloride steadily depresses the freezing point to the eutectic temperature —85°, *AB*, when the solution contains 25 per cent of HCl Further additions of hydrogen chloride raise the freezing temperature, *BC*, up to —24 4°, when the mixture contains 40 3 per cent of HCl, and thus corresponds with the trihydrate—$HCl\ 3H_2O$ Continued additions of hydrogen chloride depress the freezing point curve, *CD*, to a second eutectic —28°, and then raise it, *DE*, to a second maximum, —17 7°, corresponding with 50 31 per cent of HCl, that is, with the dihydrate—$HCl\ 2H_2O$ The freezing-point curve again descends, *EF*, to a third eutectic, —23 5°, with increasing concentration, and rises, *FG*, to a third maximum, —15 35°, when the solution contains 66 9 per cent of HCl, corresponding with the monohydrate

—$HCl \cdot H_2O$ With more concentrated solutions, the liquid separates into two layers on cooling The first eutectic is concerned with the system H_2O $HCl \cdot 3H_2O$, the second eutectic with the two hydrates $HCl.3H_2O$: $HCl \cdot 2H_2O$, and the third eutectic with the system $HCl \cdot 2H_2O$ $HCl \cdot H_2O$ Each of these three systems behaves like ice and brine indicated in Fig 54 The three maxima thus correspond with the three hydrates $HCl \cdot 3H_2O$; $HCl \cdot 2H_2O$, $HCl \cdot H_2O$ All three hydrates have been isolated in the form of white crystalline solids The existence of an octohydrate—$HCl \cdot 8H_2O$ has been inferred from the heat of solution of hydrogen chloride in water, but it is quite an imaginary hydrate, for it has not been isolated If it does exist, its presence is not indicated on the freezing point curve Fig 95 The freezing or melting point curve of a mixture of two (or more) substances is often sensitive enough to demonstrate the existence of the more stable compounds, but it is too rough and inaccurate for the less stable compounds Nevertheless, this method of investigating stable hydrates has been applied to ammonia, ferric chloride hydrates, perchloric acid, sulphuric acid, nitric acid, etc, and it has important applications in metallurgy

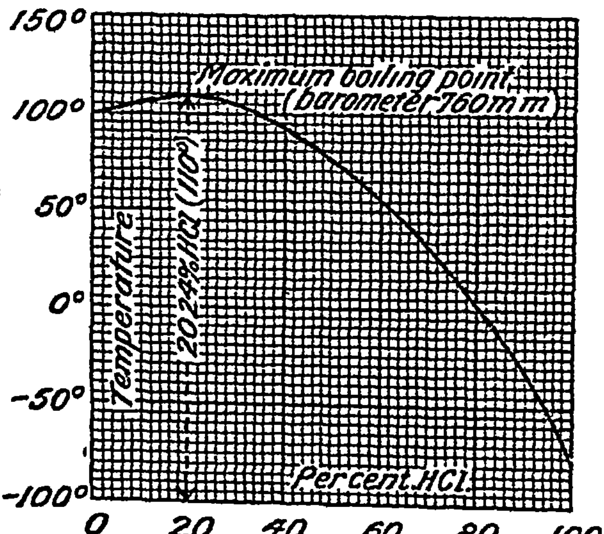


Fig 96—Boiling Points of Aqueous Solutions of Hydrogen Chloride

The effect of hydrogen chloride on the vapour pressure of water—The effect of hydrogen chloride on the boiling point of water is illustrated by the curve, Fig 96 If an aqueous solution of hydrogen chloride containing more than 20 24 per cent HCl be heated, hydrogen chloride with but little water is given off, the solution becomes less concentrated, the vapour pressure of the solution diminishes, and consequently, the boiling point rises as indicated by the curve This continues until the solution contains nearly 20 24 per cent of HCl, when its boiling point attains the maximum, 110°, any further boiling does not affect the concentration of the aqueous solution because dilute acid containing 20 24 per cent of HCl distils unchanged Again, if an acid containing less than 20 24 per cent of HCl be boiled, water accompanied by a little hydrogen chloride passes off, the boiling point of the solution gradually rises, and the solution at the same time becomes more concentrated until it contains 20 24 per cent HCl, when the acid distils over unchanged at 110° Hence 110° is the maximum boiling point of hydrochloric acid at atmospheric pressures. Similar phenomena occur with nitric and with several other acids It was once thought that the acid which corresponded with the maximum

boiling point was an octohydrate—that is, a chemical compound of hydrogen chloride and water—$HCl.8H_2O$, but since the composition of the constant boiling acid varies with the pressure,[1] and since compounds do not usually vary in composition with changes of pressure, this hypothesis has been abandoned. With solutions of oxygen, ammonia, hydrogen, and nitrogen in water the more volatile constituent leaves the solution before all the boiling water has evaporated.

Fuming liquids.—Since concentrated aqueous solutions of hydrogen chloride have a vapour pressure greater than water, we can see a reason for the fuming of hydrochloric acid in air. We know, of course, that hot water "fumes" in air because the cooler air in the vicinity of the hot water is quickly saturated with water vapour. Water at ordinary temperatures does not fume because it cannot give off more vapour than the air at the same temperature can retain. Concentrated hydrochloric acid fumes because the vapours which are given off unite with the aqueous vapour in the atmosphere to form an acid with a larger vapour pressure. Consequently, the air in the vicinity of the concentrated acid is very quickly saturated with respect to the vapour of the new acid which is formed. The new acid, in consequence, condenses to minute globules of liquid which appear as mist. Dilute acids do not fume because any vapours which they give off do not form a liquid with a greater vapour pressure than water. Hence, only those substances fume which give off vapours which unite with water to form a mixture or a compound with a greater vapour pressure than water.

The formation of chlorides.—The aqueous solution of hydrogen chloride dissolves many metals, forming chlorides and liberating hydrogen, e.g. $Zn + 2HCl = ZnCl_2 + H_2$. Zinc, magnesium, iron, aluminium, and tin are readily dissolved by cold dilute acid—the action with aluminium and tin is, however, rather slow in the cold, but much quicker in hot concentrated acid. Mercury, silver, gold, and platinum are not dissolved by the hot or cold acid; copper and lead are not dissolved by the cold dilute acid unless exposed to the air, when the action is very slow; these metals are only slowly attacked by the hot concentrated acid. Hydrochloric acid reacts with oxides, hydroxides, and carbonates producing the corresponding chlorides. Most of the chlorides are easily dissolved by water. In qualitative analysis, it is usual to divide the metals into two groups: those with soluble and those with insoluble chlorides. The "insoluble" chlorides are: silver, mercurous, cuprous, aurous, thallous, and lead chlorides. Lead chloride is, however, appreciably soluble in cold water, and much more soluble in hot water. It therefore occupies a position midway between the soluble and "insoluble" chlorides. The chloride is often more readily volatile than many of the other compounds of a given metal.

Manufacture of hydrochloric acid.—Hydrochloric acid is obtained as a by-product in the manufacture of sodium carbonate from sodium chloride. In the first stage of the process, sodium chloride is treated with sulphuric acid, and the gas which is evolved is passed up stone towers filled with lumps of coke down which a stream of water trickles. The water absorbs the gas and is collected in suitable receivers at the base of the tower.

[1] For instance, at 100 mm. pressure, the maximum boiling point is nearly 62°, and the constant boiling acid contains 22.8 per cent. HCl.

Commercial hydrochloric acid may be contaminated with ferric chloride, free chlorine, sulphurous and sulphuric acids, arsenic chloride etc The first named impurity gives commercial hydrochloric acid its yellow colour

Uses —Hydrochloric acid is used in the manufacture of chlorine, in dyeing, calico printing, the manufacture of colours, phosphates, and as a general laboratory reagent A carboy of the acid (sp gr 1 16) holds about 112 lbs —the commercial acid sells at about 8*s* per cwt , and the "pure acid" at about 2½*d* per lb pre-war prices

History —Judging from the writings attributed to Geber, hydrochloric acid was known to the early Arabian chemists, but the preparation of the pure acid—*spiritus salis*—seems to have been first described by Basil Valentine (1644) The acid appears to have been made by distilling a mixture of common salt and green vitriol (ferrous sulphate) J R Glauber (1648) described the preparation of the acid by the action of sulphuric acid on rock salt Stephen Hales (1727) noticed that a gas very soluble in water was made by heating sulphuric acid with sal ammoniac (ammonium chloride), and J Priestley about 1772, collected the gas over mercury—Priestley called the gas *marine-acid air* in reference to its mode of formation from sea salt

§ 4 The Action of Oxidizing Agents on Hydrogen Chloride

The action of oxidizing agents on hydrogen chloride or hydrochloric acid is very interesting For instance, K. W Scheele (1774) found that when hydrochloric acid is heated with manganese dioxide, a yellowish green gas, soluble in water, is given off Scheele considered the yellowish-green gas to be muriatic acid freed from hydrogen (phlogiston), that is, in the language of his time, "dephlogisticated muriatic acid" A L Lavoisier (1789) named the gas oxymuriatic acid, or oxygenated muriatic acid, because he considered it to be an oxide of muriatic (*i e* hydrochloric) acid , and, consistent with his oxygen theory of acids, p 139, Lavoisier considered muriatic acid to be a compound of oxygen with an hypothetical muriatic base—*murium* Hence, added Lavoisier, muriatic and oxymuriatic acids are related to each other like sulphurous and sulphuric acids This certainly seemed to be a most plausible explanation of the reactions Lavoisier's hypothesis was supported by an observation of C L Berthollet (1785), who noticed that an aqueous solution of oxymuriatic acid, when exposed to sunlight, gives off bubbles of oxygen gas, and forms muriatic acid

J L Gay-Lussac and J Thénard (1809) tried to deoxidize oxymuriatic acid, so as to isolate the hypothetical "muriatic base" of Lavoisier, by passing the dry gas over red hot carbon, but when the carbon was freed from hydrogen, the attempt to separate from oxymuriatic acid anything but itself was a failure While favouring Lavoisier's hypothesis, Gay-Lussac and Thénard added "the facts can also be explained on the hypothesis that oxymuriatic acid is an elementary body" Here, then, are two rival hypotheses as to the nature of oxymuriatic acid—the yellowish green gas discovered by Scheele !

In 1810, H Davy tried, without success, to decompose oxymuriatic acid He found that when hydrogen chloride is heated with metallic sodium or potassium, the metallic chloride, and hydrogen are formed, but neither water nor oxygen is obtained Davy claimed that Scheele's

view is an expression of the facts, while Lavoisier's theory, though "beautiful and satisfactory," is based upon a dubious hypothesis The definition of an element (p 12) will not permit us to assume that oxymuriatic acid is a compound, because, in spite of repeated efforts, nothing simpler than itself has ever been obtained from the gas In order to avoid the hypothesis implied in the term "oxymuriatic acid," H. Davy proposed the alternative term "chlorine" and symbol "Cl"—from the Greek χλωρὸς (chloros), green The term "chlorine" is thus "founded upon one of the obvious and characteristic properties of the gas—its colour" Lavoisier's hypothesis died a lingering death, and Davy's view is now generally adopted. According to Davy's theory, Berthollet's observation is explained by the equation $2H_2O + 2Cl_2 = 4HCl + O_2$, that is, the oxygen comes from the water, not from the chlorine Similarly, the formation of chlorine by the action of oxidizing agents upon hydrochloric acid is due to the removal of hydrogen from hydrogen chloride In symbols $4HCl + O_2 = 2H_2O + 2Cl_2$

§ 5 Chlorine—Preparation

Atomic weight, Cl = 35 46; molecular weight Cl_2 = 70 92 Generally univalent, occasionally quinque and septivalent Melting point −102°, boiling point −33 8°, critical temperature +146° Relative vapour density (H_2=2) 71 63, (air = 1) 2 49 One litre weighs 3 22 grams under normal conditions Specific gravity of liquid at 0°, 1 47

Chlorine gas is usually obtained, as indicated above, by the action of oxidizing agents—manganese dioxide, lead dioxide, barium dioxide, potassium dichromate, potassium permanganate etc —upon hydrochloric acid Scheele, the discoverer of chlorine, used a mixture of manganese dioxide and hydrochloric acid, a mixture of sodium chloride, sulphuric acid, and manganese dioxide may also be used. The mixture is heated in the apparatus illustrated in Fig 94. The action in both cases depends upon the formation of manganese trichloride, and the simultaneous oxidation of the hydrogen of hydrogen chloride $2MnO_2 + 8HCl \rightarrow 4H_2O + 2MnCl_3 + Cl_2$ When the mixture is warmed, the manganese trichloride is decomposed $2MnCl_3 \rightarrow 2MnCl_2 + Cl_2$ When this process is used on a manufacturing scale, the manganese chloride—$MnCl_2$—is treated by W Weldon's recovery process (1867) which is a modification of an earlier process by C Dunlop (1855) Air is blown through the hot residual liquid which has been previously treated with an excess of "milk of lime" In this way a considerable amount of calcium manganite—CaO MnO_2—is formed. This is called "Weldon's mud" or "manganese mud" The presence of a base is necessary for the oxidation of the oxide of manganese by air The mixture is allowed to settle, and the clear liquid run off The "mud" is gradually run into the chlorine still containing hydrochloric acid so that the "manganese" is used over and over again

Potassium permanganate is a very convenient oxidizing agent for preparing chlorine A flask containing some crystals of potassium permanganate is fitted as indicated in Fig 47, and connected with a wash-bottle containing concentrated sulphuric acid Dilute hydrochloric acid is run, drop by drop, from a tap funnel, when chlorine is evolved by the reaction . $2KMnO_4 + 16HCl \rightarrow 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2$. Chlorine is also made by the action of an excess of hydrochloric acid upon an alkaline

hypochlorite or bleaching powder The bleaching powder may be purchased compressed into cubes, with or without plaster of Paris, and used in Kipp's apparatus, Fig 12, with hydrochloric acid (L Winkler, 1887) The gas attacks mercury, and it is not, therefore, collected in the mercury trough, it is also fairly soluble in water and the solution is rather unpleasant For general laboratory work the gas can be collected over hot water saturated with salt, or better, by the upward displacement of air in the stink closet.

Gold and platinum chlorides give off chlorine when heated, but these compounds are too expensive for the preparation of chlorine, except for very special work, such as V Meyer's work on the vapour density of chlorine, where platinous chloride was used as the source of chlorine Cupric chloride—$CuCl_2$—also gives off chlorine when heated. $2CuCl_2 = 2CuCl + Cl_2$, and this method is sometimes used for the preparation of pure chlorine In W Weldon and A R Péchiney's process (1883) for chlorine, magnesium chloride is heated in a current of air Magnesium oxide and free chlorine are produced $2MgCl_2 + O_2 = 2MgO + 2Cl_2$ The oxide of magnesium is then treated with hydrogen chloride to regenerate magnesium chloride $MgO + 2HCl = H_2O + MgCl_2$ The chloride so formed is again heated in a current of air, so that the process of manufacture of chlorine is continuous.

Deacon's process for chlorine—The oxidation of hydrogen in hydrogen chloride can be effected by atmospheric oxygen, by passing the mixed gases through a tube at a high temperature The action takes place below 400° in the presence of pumice stone saturated with cuprous chloride—$CuCl$ The result of the reaction is represented by the equation: $4HCl + O_2[+ CuCl] = 2H_2O + 2Cl_2[+ CuCl]$ The cuprous chloride remaining at the end of the reaction has the same composition as at the beginning It is supposed that the first action results in the formation of a copper oxychloride $\{4CuCl + O_2 = 2Cu_2OCl_2$, followed by $Cu_2OCl_2 + 2HCl = 2CuCl_2 + H_2O$, and finally by $2CuCl_2 = 2CuCl + Cl_2\}$ The chlorine is necessarily contaminated with undecomposed hydrogen chloride, atmospheric nitrogen, atmospheric oxygen, and steam. The steam and hydrogen chloride can be removed by washing, etc The chlorine so prepared is used in the manufacture of bleaching powder, where the presence of the impurities does no particular harm This is the principle of H W Deacon's process (1868) The reaction can be illustrated by the apparatus shown in Fig 97 Air is forced from a gas holder through a hot solution of concentrated hydrochloric acid The mixture of air and hydrogen chloride so obtained is passed through a wash-bottle containing water, and then through a hot porcelain tube containing pumice stone impregnated with a solution of cupric chloride and dried The chlorine gas obtained at the exit can be collected in the usual manner It is of course mixed with the excess of air, nitrogen, etc

In the reaction $4HCl + O_2 = 2Cl_2 + 2H_2O$, both chlorine and oxygen are competing for the hydrogen, at 577° both appear equally strong, for the hydrogen is distributed equally between the chlorine and oxygen At higher temperatures the chlorine is stronger than oxygen, because less free chlorine is obtained than at lower temperatures, when the affinity of oxygen for the hydrogen is the stronger. In consequence,

a greater yield of free chlorine is obtained at temperatures lower than 577°. The temperature, however, cannot be reduced indefinitely because the reaction would then become inconveniently slow, even in the presence of the catalytic agent—cuprous chloride. The catalytic agent begins to volatilize at temperatures even below 430°.

Electrolytic processes for chlorine and alkaline hydroxides.—If an aqueous solution of potassium chloride or sodium chloride be electrolyzed, chlorine (anion) appears at the anode, and the metal (cation) at the cathode. In the case of sodium chloride, we have $NaCl = Na + Cl$. The metal then reacts with the water, liberating hydrogen and forming sodium hydroxide. The net result of the electrolysis is: $2NaCl + 2H_2O = Cl_2 + H_2 + 2NaOH$, so that hydrogen gas appears at the cathode and

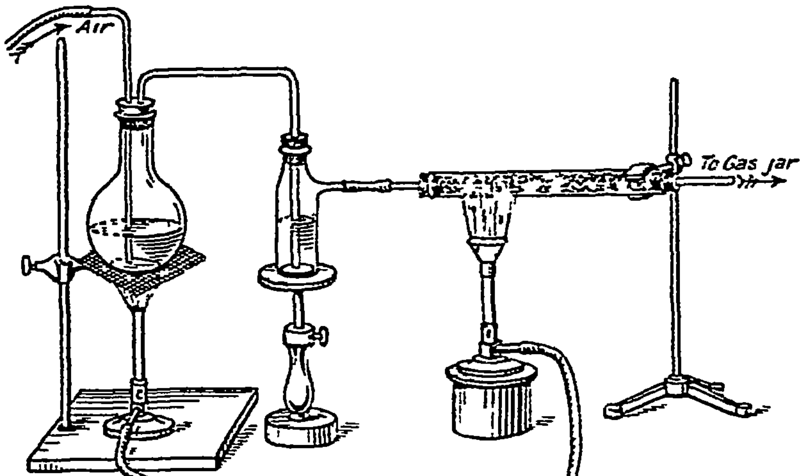


FIG. 97.—Illustration of Deacon's Process for Chlorine.

chlorine at the anode. The two electrodes must be separated to prevent the sodium hydroxide formed at the cathode mixing with the chlorine discharged at the anode. The separation is effected:—

(1) *Diaphragm process.*—By using a porous diaphragm—Portland cement, earthenware, asbestos, limestone, etc. This permits electrolytic conduction, and prevents the solutions mixing but very slowly.—P. Matthes and Weber, 1886.

(2) *Bell process.*—By enclosing the anode in an inverted non-conducting bell with the cathode outside.—W. Bein, 1893.

(3) *Mercury cathode process.*—The sodium is dissolved by the mercury to form an amalgam. The amalgam is removed from the cell and treated with water, when sodium hydroxide and mercury are obtained. The mercury is returned to the cell to be used over and over again.—E. Solvay's process, 1898.

(4) *Mercury diaphragm process.*—By the use of a mercury diaphragm as in H. Y. Castner's process, 1893, illustrated in Fig. 98. The cell has three compartments. The two outer compartments are fitted with graphite anodes (+), and the middle compartment is fitted with an iron

grid (—) to serve as cathode The non-porous partitions do not reach quite to the bottom of the cell but dip into a layer of mercury covering the bottom A solution of alkali chloride flows through the two outer cells, and water through the inner compartment The brine in the outer compartment is decomposed by the electric current into chlorine at the anode and sodium at the cathode The latter dissolves in the mercury, at the cathode, and the chlorine at the anodes escapes *via* the exit pipes. The sodium amalgam diffuses into the inner chamber and there, coming into contact with the water, is immediately decomposed into sodium hydroxide and mercury. The hydrogen escapes through the loosely fitting cover. The sodium hydroxide is run into a special tank as required. A slow rocking motion is imparted to the cell during the electrolysis, by an eccentric wheel, so as to make the mercury flow from one compartment to the other along the bottom of the cell.

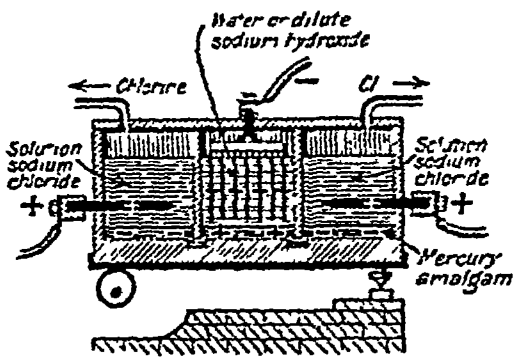


FIG 98 —Castner's Mercury Diaphragm Process

(5) *Fused electrolytic* —In Acker's process (1898), now abandoned, molten lead was used as anode for collecting the sodium The alloy of lead and sodium was decomposed by steam to form hydrogen and sodium hydroxide Fused alkaline chlorides also furnish chlorine when electrolyzed. Pure chlorine, for special experiments, has been made by the electrolysis of pure fused silver chloride with carbon electrodes. For the electrolysis of hydrochloric acid, see p 240

§ 6 Chlorine—Properties

Chlorine is a yellowish-green gas with an irritating smell It attacks the membrane of the throat, lungs, and nose If a little be breathed for some time, it causes an irritating cough attended by the spitting of bloody mucous Larger quantities of chlorine are fatal Chlorine is about $2\frac{1}{2}$ times as heavy as air, and being slightly soluble in cold water, it can be collected by the upward displacement of air, over hot water or over a concentrated solution of salt in which it is not so very soluble

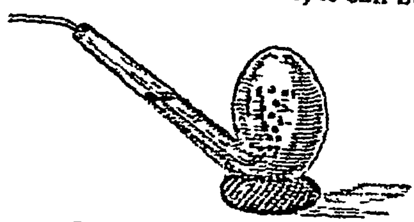


FIG 99 —Preparation of Chlorine Water

The action of chlorine on water.—100 volumes of water at 0° dissolve 461 volumes of the gas, and at 20°, 22 6 volumes The solution in water—chlorine water—is yellowish-green in colour, and it has the taste and smell of chlorine itself Chlorine water is conveniently made by passing the gas into an inverted retort, placed as illustrated in Fig 99 When the water is cooled by surrounding it with melting ice, yellow rhombic octahedral crystals of chlorine octohydrate—$Cl_2.8H_2O$—separate. The

hydrate decomposes slowly at temperatures just over 0°, and rapidly at higher temperatures Thus the vapour pressure of the hydrate at 0° is 250 mm, at 5°, 481 mm, and at 10°, 832 mm If the hydrate be sealed in a tube, it will melt at ordinary temperatures, forming two liquids—an upper aqueous layer, and a lower layer containing most of the chlorine

The liquefaction of chlorine.—On March 5, 1823, M Faraday was operating with chlorine hydrate in a sealed tube Dr J A Paris called at the laboratory and noticed some oily matter in the tube Faraday was using, he rallied Faraday "upon the carelessness of employing soiled vessels" Faraday started to open the tube by filing the sealed end, the contents of the tube suddenly exploded, and the "oil" vanished. Faraday repeated the experiment, and Dr Paris, next morning, received the laconic note —

> "Dear Sir,—The *oil* you noticed yesterday turned out to be liquid chlorine —Yours faithfully, MICHAEL FARADAY"

Chlorine can be condensed to a golden-yellow liquid at 0° and 6 atmospheres pressure By sealing chlorine hydrate in one limb of a Λ-shaped tube, and placing that leg in warm water while the other leg is immersed in a freezing mixture (Fig 100) of, say, ice and salt, yellow oily drops of liquid chlorine condense in the cold limb The liquid boils at −33·6° under atmospheric pressure, and freezes to a pale yellow crystalline mass which melts at −102° Liquid chlorine is sold commercially in steel cylinders

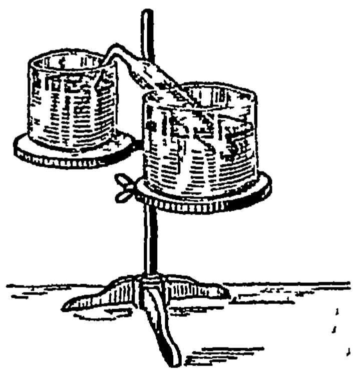


FIG 100.—Liquefaction of Chlorine

The action of chlorine on other elements.—Thoroughly dry chlorine is somewhat inert chemically, and it has no appreciable action upon bright metallic sodium, copper etc Moist chlorine is particularly active Chlorine does not combine with oxygen directly although several compounds of chlorine and oxygen can be obtained indirectly (The inert gases, nitrogen, oxygen, carbon, and some of the rarer platinum metals, resist attack by *free* chlorine) The direct union of many of the elements with chlorine is attended by incandescence—for instance, powdered antimony, arsenic, and bismuth when shaken into a flask containing chlorine Since the chlorides of antimony, etc, so formed are poisonous, the experiments are best made in a closed system, illustrated Fig 101 When the bulb tube containing the powdered element is raised, it is easy to shake the contents through the flask of chlorine to illustrate the incandescence which attends the combustion without an escape of the poisonous chlorides into the atmosphere of the room Copper, brass foil, Dutch metal, phosphorus, boron, and silicon also ignite spontaneously in chlorine. Molten sodium hot brass wire, and iron wire also burn in chlorine

In sunlight, equal volumes of hydrogen and chlorine combine with explosion The same remark applies when a mixture is exposed to the light of burning magnesium Let a jar of hydrogen and a similar jar of

chlorine be placed mouth to mouth (Fig 34), the gases well mixed, the jars separated and immediately covered with greased glass plates When a lighted taper is applied to the mouth of one jar, the gases unite with explosion A piece of cold but recently ignited charcoal placed in the other jar frequently causes the gases to combine with explosive violence

Hydrogen does not appear to combine with chlorine with appreciable velocity in the dark, but in diffused daylight, the two slowly combine to form hydrogen chloride The speed of the reaction is proportional to the intensity of the light Hence, actinometers have been designed to measure the intensity of light in terms of the speed of combination of a mixture of hydrogen and chlorine gases If light be filtered through a layer of chlorine gas before it impinges on the mixture of hydrogen and chlorine, the light produces no appreciable effect Insolated chlorine rises slightly in temperature, even when the heat rays have been filtered from the incident light It is therefore inferred that *actinic (light) energy absorbed by chlorine is at once degraded into thermal energy If hydrogen be associated with the chlorine, when exposed to light, the process of degradation of the actinic energy is accompanied by chemical action* (J W Mellor, 1902) The presence of minute traces of impurities in the gases retards the rate of combination in a remarkable way

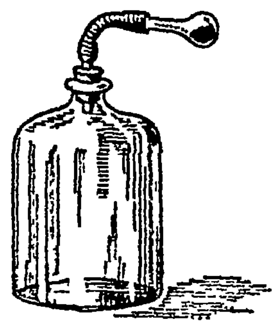


FIG 101 —Combustion of Antimony, etc, in Chlorine

A jet of burning hydrogen lowered into a jar of chlorine continues burning with the formation of hydrogen chloride Chlorine gas may also be burnt in an atmosphere of hydrogen Hydrocarbons are decomposed by chlorine, for instance, a piece of cotton wool soaked in warm turpentine ($C_{10}H_{16}$) will inflame when placed in a jar of chlorine The burning of the turpentine is accompanied by the separation of dense clouds of free carbon The chlorine combines with the hydrogen forming hydrogen chloride, and carbon is set free A wax candle burns in chlorine with a very smoky flame, the hydrocarbon—wax—is decomposed in a similar manner See also Fig 201 Hence, chlorine may be regarded as non-combustible, and a supporter of combustion

Oxidizing effects of chlorine —Moist chlorine, or chlorine water, is a powerful oxidizing agent We have seen that chlorine water is decomposed in sunlight, p 234. Oxygen gas is given off and hydrogen chloride is formed $2H_2O + 2Cl_2 = 4HCl + O_2$ If a piece of coloured litmus paper, coloured petals of a flower, or a piece of cloth dyed with turkey red or indigo blue be placed in a jar of dry chlorine no appreciable change occurs, but if moisture be present, the colours are bleached by the chlorine The action appears to be due to the formation of a colourless oxidation product Ordinary oxygen will not do the work of bleaching It is therefore assumed that the oxidation is effected by the nascent oxygen—p 292, another that it is due to the decomposition of hypochlorous acid formed by the action of chlorine on water

Dissociation of the chlorine molecule —The density of chlorine below 600° corresponds with 70·92, and the molecule is accordingly Cl_2, at higher temperatures, the density assumes lower values. At 1200°, the density is

47 3, that is, about two thirds the normal value for chlorine This is explained by the assumption that the two atom chlorine molecules commence to dissociate into one atom molecules above 600° $Cl_2 \rightleftharpoons Cl + Cl$.

Uses —Chlorine is used in the manufacture of bleaching powder, in the extraction of gold, in bleaching—*e g* wood pulp, etc., in the manufacture of bromine, etc

§ 7 The Composition of Hydrogen Chloride and the Atomic Weight of Chlorine

1 **Analysis of hydrogen chloride by sodium amalgam.**—A stoppered glass tube—about 70 cm long and 1 5 cm. in diameter —is filled with dry hydrogen chloride over mercury Sodium amalgam is then dropped into the tube, and the tube *immediately* closed with its stopper The tube is inverted several times in succession, and then opened while its mouth is dipping under mercury Mercury rushes into the tube, and the residual gas is brought under atmospheric pressure by raising or lowering the tube until the mercury inside and outside is at the same level (Fig 102) The volume of the residual gas is noted. The residual gas can then be tested in the usual manner It is hydrogen The hydrogen chloride reacts with the sodium of the mercury amalgam forming sodium chloride and liberating hydrogen The object of using sodium amalgam in place of metallic sodium is one of convenience This experiment demonstrates that hydrogen chloride contains half its own volume of hydrogen. Hence, from Avogadro's hypothesis one molecule of hydrogen chloride contains half a molecule, that is, one atom of hydrogen The formula is therefore HCl_x, where x represents the number of atoms of chlorine in the molecule The vapour density of hydrogen chloride is nearly 36 5 ($H_2 = 2$) Hence the molecular weight is 36 5, and the weight of hydrogen in the molecule is 1 The molecule of hydrogen chloride thus contains 36 5 − 1 = 35 5 parts of chlorine This is the atomic weight of chlorine Hence the formula for hydrogen chloride is HCl

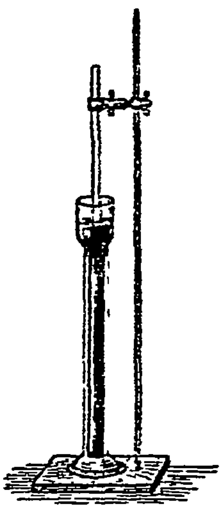


FIG 102 —Volume Composition of Hydrogen Chloride

2 **The electrolysis of hydrochloric acid** —When concentrated hydrochloric acid is electrolyzed, a mixture of equal volumes of hydrogen and chlorine is obtained Carbon electrodes are used because the chlorine slowly attacks platinum. Chlorine gas is also soluble in concentrated hydrochloric acid, so that the acid should be saturated with chlorine before the attempt is made to measure the gaseous products of electrolysis If the vessel containing the acid is arranged so that the acid about one electrode is connected with the acid about the other electrode by a glass tube junction, Fig 103, it is only necessary to saturate the solution about one electrode with chlorine The apparatus illustrated, Fig 103, devised by L. Meyer, has two limbs filled with concentrated hydrochloric acid, and an

electric current is passed until the liquid in the chlorine limb is saturated with chlorine The two gas receivers are put into communication with the electrolytic vessel by suitably turning the three-way stopcocks The gas receivers have, of course, been previously filled with liquid—a saturated solution of sodium chloride—by placing a dish of the liquid below each receiver and applying suction at the proper exit tube when the three-way cocks are suitably turned The gases collect in the tubes at equal rates The experiment shows that during the electrolysis of concentrated hydrochloric acid, the volume of hydrogen liberated at the one electrode is equal to the volume of chlorine liberated at the other electrode Assuming that the hydrogen chloride dissolved in the water is alone decomposed by the electric current it follows that hydrogen chloride contains equal volumes of hydrogen and of chlorine, and therefore also an equal number of atoms, or the formula is H_xCl_x, where x is evaluated as before from the vapour density 36 5 This demonstration of the composition of hydrogen chloride, though interesting as circumstantial evidence, is not a *proof* unless supported by accessory evidence A similar demonstration applied to the analogous hydrofluoric acid would "prove" that hydrogen fluoride is a compound of hydrogen and oxygen

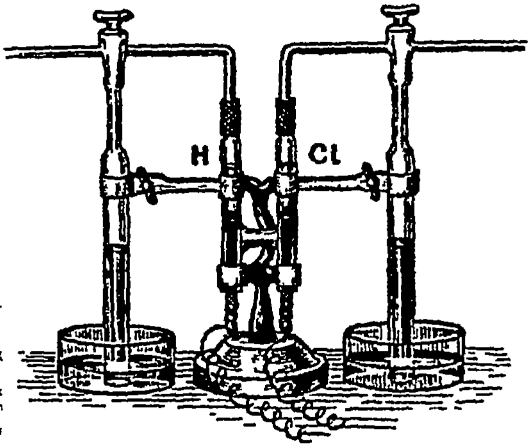


FIG 103 —Meyer's Apparatus for the Electrolysis of Hydrochloric Acid

When concentrated acid is diluted with eight volumes of water and electrolyzed, some oxygen is evolved along with the chlorine, with nine volumes of water, still more oxygen is evolved. The more dilute the acid the greater the amount of oxygen, until, with water acidified with a few drops of acid, no chlorine, but oxygen alone is obtained at the anode, p 51

3 The synthesis of hydrogen chloride —The mixed gases obtained by the electrolysis of concentrated hydrochloric acid in an apparatus resembling Fig 18 are passed through a stout glass "explosion" tube with a stopcock at each end, *A*, Fig 104 The tower is packed with lime and glass wool to absorb the chlorine Instead of this the exit tube may lead to the fume closet When all the air is displaced, the stopcocks are closed One of the stopcocks may be opened while the corresponding end of the tube is dipping under concentrated sulphuric acid, no gas enters or leaves the apparatus The tube and contents are exposed to sunlight or to the light from burning magnesium The face must be protected in case the tube should burst during the explosion When the

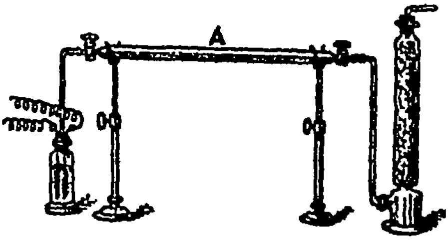


FIG 104 —Collecting Electrolytic Hydrogen and Chlorine

tube is cold, open one of the stopcocks while the corresponding end is dipping under concentrated sulphuric acid, no gas enters or leaves the tube This shows that no change in volume has taken place as a result of the explosion It can be proved that the tube contains nothing but hydrogen chloride by opening the tip of the tube under water The hydrogen chloride will be absorbed and water will rise and fill the tube except for a little air (or perhaps a slight excess of hydrogen) which might have been present This experiment shows that **one volume of hydrogen unites with one volume of chlorine to form two volumes of hydrogen chloride**

Hydrogen chloride contains the equivalent of half its volume of chlorine and half its volume of hydrogen, or, by Avogadro's hypothesis, assuming the hydrogen and chlorine each contain two atoms, one molecule of hydrogen chloride contains half a molecule of hydrogen and half a molecule of chlorine, that is, one molecule of hydrogen chloride contains an atom of chlorine and an atom of hydrogen The formula is therefore HCl This agrees with the vapour density determination of hydrogen chloride which furnishes 36 49 ($H_2 = 2$) If the atomic weight of chlorine be 35 46, and of hydrogen 1 008 (O = 16), it follows that the formula for hydrogen chloride is HCl

4 **The atomic weight of chlorine** —The combining weight of chlorine has been deduced by finding how much silver chloride can be obtained from a given amount of silver The results show that Ag Cl = 107 88 35 46 The ratio H Cl has also been determined by the combustion of hydrogen in chlorine in an apparatus similar in principle to that employed by Morley for the combustion of hydrogen in oxygen, p 46 Collecting the best determinations, it is found that the ratio varies between 1 35 43 and 1 35 46 The best representative value is taken to be 35 46 Again collecting together the vapour density determinations of all known volatile chlorides we obtain a table from which the following has been abstracted

TABLE IX —MOLECULAR WEIGHTS OF VOLATILE COMPOUNDS.

Volatile chloride	Vapour density	Formula of compound molecular weight = vapour density	Amount of chlorine in the molecule
Hydrogen chloride	36 5	HCl	35 46
Chlorine	70 9	Cl_2	70 92
Mercuric chloride	273 6	$HgCl_2$	70 92
Arsenic trichloride	182 1	$AsCl_3$	106 38
Tin tetrachloride	260 2	$SnCl_4$	141 84
Phosphorus pentachloride	208 3	PCl_5	177 30

The smallest combining weight of chlorine in any one of these compounds corresponds with the combining weight 35 46—oxygen = 16—and accordingly this number is taken to represent the atomic weight of chlorine The atomic and equivalent weights of chlorine have the same numerical value

§ 8 The Chlorides of Calcium, Barium, Magnesium, and Zinc.

Many metals readily combine with chlorine, forming chlorides, and often in several different proportions e g stannous chloride, $SnCl_2$, and stannic chloride, $SnCl_4$, cuprous chloride, CuCl, and cupric chloride, $CuCl_2$, mercurous chloride, HgCl, and mercuric chloride, $HgCl_2$, ferrous chloride, $FeCl_2$, and ferric chloride, $FeCl_3$, etc

In addition to the methods of making chlorides previously described, namely, by acting on the metal, the metallic oxide, hydroxide, or carbonate with hydrochloric acid, and by adding a soluble chloride to a solution of the metallic salt whereby a sparingly soluble chloride is precipitated, chlorides can be made by the action of chlorine on the metallic oxide, or a mixture of the metallic oxide with carbon, or by the action of chlorine

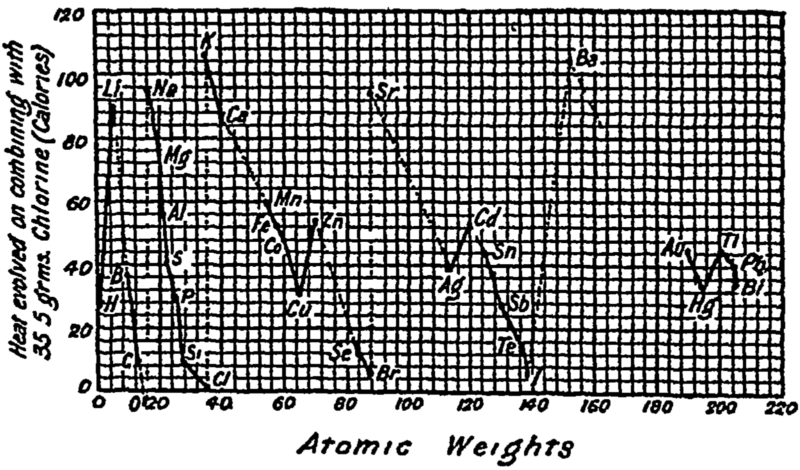


FIG 105 —Heats of Formation of the Chlorides (A P Laurie, 1882).

or hydrogen chloride on the metal, and by some other methods to be described later These last processes are generally used when an anhydrous chloride is wanted

Calcium, strontium, barium, magnesium, zinc, cadmium, and beryllium chlorides form a closely graded series They can all be made by the general methods, and they all crystallize from aqueous solutions united with water which varies from one to seven molecules of water per molecule of the chloride For instance, $ZnCl_2$, H_2O; $BaCl_2$, $2H_2O$, $CaCl_2$, $6H_2O$, etc The mode of combination of the water molecules, generally called water of crystallization, is not clear It is sometimes supposed to depend upon the quadrivalency of the oxygen of the water molecule, and the tervalency of chlorine Thus:

$$Zn{<}^{Cl}_{Cl}{>}O{<}^{H}_{H}$$

If the heats of combination of the different elements with chlorine be plotted with the atomic weights of the elements, a curious periodic curve is obtained as indicated in Fig 105, where the dotted lines denote the want of data

Double chlorides—The chlorides may also unite with other chlorides forming double chlorides, e g $MgCl_2.NH_4Cl.6H_2O$, $MgCl_2.KCl.6H_2O$, $ZnCl_2.NH_4Cl$, etc, when their mixed aqueous solutions are concentrated and allowed to crystallize The double chlorides can be dried without decomposition This property is not so well defined with the calcium, barium, and strontium compounds as with beryllium, zinc, cadmium, and magnesium compounds The property has been attributed to the multivalency of chlorine Thus, with tervalent chlorine

$Zn{<}^{Cl}_{Cl}$	$Zn{<}^{Cl=Cl-K}_{Cl=Cl-K}$
Zinc chloride	Zinc potassium chloride

Hydrolysis—These chlorides are slightly decomposed in aqueous solutions The term "hydrolysis" is generally employed for the interaction between a salt and water whereby free acid and free base, or an acid and a basic salt are formed Hydrolysis is thus a kind of reversion of the process of neutralization of an acid with a base, or of base with an acid In the case of magnesium chloride and water, a certain amount of the magnesium chloride is decomposed, and magnesium hydroxide and hydrochloric acid are formed $MgCl_2 + 2H_2O \rightleftharpoons Mg(OH)_2 + 2HCl$, or possibly $MgCl_2 + H_2O \rightleftharpoons Mg(OH)Cl + HCl$ The amount of hydrolysis in aqueous solutions of barium, strontium, and calcium chlorides is insignificant, although these salts, as well as the alkaline chlorides, are very slightly hydrolyzed The hydrolysis of sodium chloride can be demonstrated by Emich's experiment

✓ Heat a little sodium chloride in a platinum crucible to bright redness, and add a couple of drops of water to the hot crucible so that the water assumes the spheroidal state In a moment, transfer the water to a beaker containing a very faintly coloured solution of blue litmus—the litmus is reddened showing the presence of an acid—hydrochloric acid The salt remaining in the crucible is dissolved in water, and it turns red litmus blue, showing the presence of an alkali—sodium hydroxide

Hydrolysis belongs to the type of "opposing reactions" previously discussed Equilibrium occurs when the speed of hydrolysis is equal to the speed of re combination of the products of the hydrolysis If one or both the products of hydrolysis are removed from the sphere of the reaction, either by the formation of a precipitate, or by the liberation of a gas, the whole of the salt may be hydrolyzed With bismuth chloride, $BiCl_3$, for example, the basic salt $BiCl(OH)_2$ is quantitatively precipitated $BiCl_3 + 2H_2O \rightleftharpoons BiCl(OH)_2 + 2HCl$ This reaction, in fact, is one of the standard methods employed in analysis for the quantitative precipitation of bismuth quantitatively from a solution

✓ In consequence of hydrolysis, when aqueous solutions of zinc or magnesium chlorides are concentrated by evaporation, some hydrogen chloride volatilizes, and a mixture of the oxide and chloride, or a basic compound—Mg_2OCl_2, or $MgO.MgCl_2$—is formed The anhydrous chloride cannot therefore be prepared by the evaporation of the aqueous solutions. If hydrogen chloride be prevented from leaving the solution by conducting the evaporation in a stream of hydrogen chloride, the hydrolysis of the magnesium chloride cannot proceed very far Indeed, the excess of hydrogen chloride drives the hydrolysis backwards by increasing the concentration of hydrogen chloride in the system, so that it is possible to

prepare anhydrous magnesium chloride by the evaporation of aqueous solutions in a stream of hydrogen chloride gas See "zinc sulphate" for another view of hydrolysis

Magnesium and zinc oxychlorides.—When magnesium chloride is heated in air, chlorine is evolved, and magnesium oxychloride, Mg_2OCl_2, is formed, and at still higher temperatures, nearly all the chloride is decomposed and magnesium oxide, MgO, remains See Weldon and Péchiney's process for chlorine, p 235

If calcined magnesia be made into a thick paste with a concentrated solution of magnesium chloride, or if zinc oxide and zinc chloride be treated in a similar manner, the mass hardens to a stone-like mass owing to the formation of an oxychloride Hence the use of these mixtures as cements *e.g* zinc oxychloride is employed by dentists for stopping teeth, and magnesium oxychloride—*Sorel's cement*, or *magnesia cement*—is used in the manufacture of artificial stones, tiles, etc

Solubility of the chlorides in water.—When the anhydrous chlorides are dissolved in water, heat is evolved, and the solution becomes warmer *e.g* $CaCl_2 + Aq = CaCl_{2aq} + 17 \cdot 4$ Cals, with anhydrous barium chloride, 2 1 Cals, and with anhydrous magnesium chloride, 436 0 Cals On the contrary, when the crystalline hydrates are dissolved in water, heat is absorbed, and the solution becomes cooler *e.g* $CaCl_2 6H_2O + Aq = CaCl_{2aq} - 4 \cdot 3$ Cals, with crystalline barium chloride $BaCl_2 2H_2O - 4 \cdot 9$ Cals, and with crystalline magnesium chloride, $MgCl_2.6H_2O - 3 \cdot 0$ Cals. Thus, the temperature can be reduced from 0° to −42° by a mixture of 2 parts of crystallized calcium chloride, with half its weight of snow or powdered ice, 3 parts of potassium chloride with 2 parts of snow will lower the temperature from 0° to −33°, and with 10 parts of snow, from 0° to −11°; 1 part of sodium chloride with 3 parts of snow will lower the temperature from 0° to −17 7° Hence the use of such salts as freezing mixtures

It is well to remember that the dissolution of a solid is attended by (1) the separation of the molecules against molecular attraction, (2) the liquefaction of the solid, and (3) combination of the solute with the solvent The two former involve an expenditure of energy and exercise a cooling effect, the last alone usually exercises a heating effect, whether the dissolution of a solid will be an endo- or an exo-thermal process is thus determined by the relative magnitudes of these three effects When liquids are dissolved, (2) will be zero, and with gases liquefaction will be attended by an evolution of heat

An idea of the solubility of the chlorides of barium ($BaCl_2$), strontium ($SrCl_2$), calcium ($CaCl_2$), cadmium ($CdCl_2$), magnesium ($MgCl_2$), and zinc ($ZnCl_2$), will be obtained from the following table which represents the amount of salt, in grams, dissolved by 100 grams of water at the temperatures named

TABLE X.—SOLUBILITIES OF CHLORIDES

Temperature	$BaCl_2$	$SrCl_2$	$CaCl_2$	$CdCl_2$	$MgCl_2$	$ZnCl_2$
0°	32	43	59	9	53	208
50°	44	72	126	10	60	470
100°	59	102	155	14	73	615

The remarkable solubility of zinc chloride is worthy of special note At 50°, for instance, zinc chloride forms a thick syrupy liquid with one fourth of its weight of water The great affinity of zinc and calcium chlorides (anhydrous) for water is utilized in chemical work Calcium chloride is extensively employed in the laboratory for drying gases, and zinc chloride is a powerful dehydrating agent It decomposes many organic compounds, taking from them the elements of water Zinc chloride is also used as an antiseptic, in the preservation of wood from decay, and owing to its power of dissolving metallic oxides, as a flux in soldering

The smoothing of solubility curves—The solubility curves of these salts would be misleading if plotted from the numbers indicated above, for many of these chlorides give solubility curves with a number of breaks which would thus be smoothed out and accordingly obscured Care must always be exercised in smoothing data obtained at widely differing temperatures, because some important phenomena may thus be masked The breaks correspond with the change in the solubility which attends the transformation of one hydrate into another as the temperature rises Calcium chloride may be taken to illustrate the principle, Fig 106 At 29.8° the hexahydrate $CaCl_2 \cdot 6H_2O$ changes into the α tetrahydrate α $CaCl_2 4H_2O$, at 45.3° the α tetrahydrate passes into the dihydrate $CaCl_2 2H_2O$, at 175.5° (not shown in the diagram) the dihydrate passes into the monohydrate $CaCl_2 H_2O$, and at 260° the monohydrate passes into the anhydrous salt $CaCl_2$ The changes from one hydrate to the other produce the breaks, some of which are indicated in Fig 106 Each hydrate has its own particular solubility curve There are two different tetrahydrates, each having its own specific solubility curve They are distinguished as the α and the β tetrahydrates, the former being the stable hydrate whose solubility curve is shown in the diagram

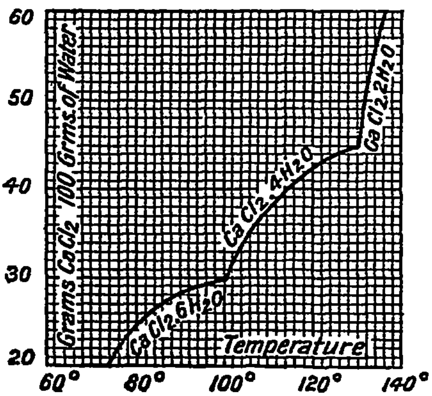


FIG 106 —Solubility Curve of Calcium Chloride

Deliquescence and efflorescence—Each hydrate has its own specific vapour pressure at a particular temperature The average vapour pressure of the water vapour in atmospheric air is equivalent to 8 or 9 mm of mercury If the vapour pressure of the hydrate be greater than the vapour pressure of atmospheric moisture, the hydrate will *lose* water on exposure to the air—in other words, the salt will effloresce, on the contrary, if the vapour pressure of the hydrate be less than that of the atmospheric moisture, the salt will *absorb* moisture from the atmosphere, and deliquesce Here are a few illustrations

TABLE XI.—VAPOUR PRESSURES OF HYDRATES

Salt	Vapour pressure mm	Property
$CaCl_2.6H_2O$	3.2	Deliquescent
$FeCl_3.6H_2O$	6.0	Deliquescent
$Na_2SO_4.10H_2O$	27.8	Efflorescent
$Na_2CO_3.10H_2O$	24.2	Efflorescent

It is therefore possible to predict whether or not a salt will have a tendency to efflorescence or deliquescence when the vapour pressure of the hydrate is known. But a perfectly sound crystal of, say, sodium sulphate does not effloresce on exposure to the atmosphere. If, however, the change has commenced at any point, it will spread throughout the whole mass. This is in accord with the phase rule $F = C - P + 2$. In the perfect crystal there are two phases P, namely sodium sulphate, $Na_2SO_4.10H_2O$, and water vapour, and two components C, namely Na_2SO_4 and H_2O. Hence the system is bivariant ($F = 2$), so that the pressure of the water vapour and the temperature can vary arbitrarily within certain limits without altering the state of the system. If, however, some efflorescent salt be present, there will be three phases, and the system will be univariant ($F = 1$), so that for every temperature there is one and only one vapour pressure for equilibrium.

Manufacture of calcium and barium chlorides.—Calcium chloride is obtained as a by-product in many manufacturing operations—manufacture of potassium chlorate, of ammonia from ammonium chloride, etc. The salt crystallizes from its aqueous solutions in hexagonal crystalline prisms. Barium chloride is made by dissolving witherite, native barium carbonate, in hydrochloric acid. It is also manufactured from the mineral barytes, barium sulphate, $BaSO_4$, by roasting the mineral with powdered coke, limestone, and calcium chloride. The barium sulphate is reduced to the sulphide, BaS, thus $BaSO_4 + 4C = BaS + 4CO$. The barium sulphide then reacts with the calcium chloride, forming calcium sulphide and barium chloride: $BaS + CaCl_2 = CaS + BaCl_2$. The mass is lixiviated with water; the calcium sulphide remains behind, and barium chloride passes into solution. When the solution is concentrated and cooled, barium chloride, $BaCl_2.2H_2O$, separates in colourless rhombic plates.

§ 9. Mercury, Silver, Copper, and Gold Chlorides

Mercury, silver, copper, and gold form a series of chlorides—HgCl, CuCl, AgCl, AuCl—similar in type to the alkaline chlorides—KCl, NaCl—but they are all very sparingly soluble in water. In these chlorides the metal appears to behave as a monad; but, in addition, mercury and copper respectively form $HgCl_2$ and $CuCl_2$, in which the metals behave as dyads; gold also forms a second chloride—$AuCl_3$—in which the metal behaves as a triad. The lower chlorides are named mercurous, cuprous, and aurous chlorides; and the higher chlorides are called mercuric, cupric, and auric chlorides.

Mercuric chloride $HgCl_2$—also called *corrosive sublimate*—is made on a commercial scale by heating a mixture of mercuric sulphate with sodium chloride $2NaCl + HgSO_4 = Na_2SO_4 + HgCl_2$, a little manganese dioxide, MnO_2, is usually added with the object of preventing the formation of the lower chloride Mercuric chloride sublimes as a white translucent mass The salt can be obtained in needle like rhombic prisms by cooling a solution saturated with the salt at 100° There is a great difference in the solubility of the salt at 100° and at lower temperatures, thus 100 grams of solution at 0° contains 3 5 grams of salt, and at 100°, 38 grams The salt melts at 288° and vaporizes about 300° Like magnesium and zinc chlorides, mercuric chloride readily forms mercuric oxychloride and also double salts, *e.g* $HgCl_2.HCl$, $HgCl_2.H_2O$, etc, that last named is the "sel alembroth" of the early chemists The double salts are more soluble than mercuric chloride, and they are much used in making antiseptic solutions for taxidermists, etc Mercuric chloride is a valuable antiseptic, and is used for washing wounds, etc, in surgery Dilute solutions, 1 part of salt per 1000 parts of water, or per 2000 parts of water, are usually employed. Mercuric chloride is a virulent poison The antidote is albumen (the white of a raw egg) This forms with the salt an insoluble mass which can be removed from the stomach

Mercurous chloride, HgCl or Hg_2Cl_2—also called *calomel* If mercuric chloride be heated along with metallic mercury, a sublimate of mercurous chloride is obtained as a white powder The mixture used for the preparation of mercuric chloride can also be employed if the manganese oxide be omitted, and metallic mercury introduced $HgCl_2 + Hg = 2HgCl$ Mercurous chloride can also be made by the direct union of mercury and chlorine, and by the addition of a soluble chloride, or, better, hydrochloric acid, to a soluble mercurous salt. Mercurous chloride is precipitated One litre of water dissolves but 0 002 gram of mercurous chloride at 18° Mercurous chloride slowly blackens when exposed to light This is said to be due to the reversal of the reaction just indicated The blackening is thus due to the separation of mercury The salt is also blackened by contact with alkalies and aqueous ammonia—hence the term "calomel" from the Greek καλομελας (kalomelas), black. This black powder appears to be mercuric amido-chloride, $Hg(NH_2)Cl$ mixed with metallic mercury and the reaction is represented

$$\begin{matrix} Hg—Cl \\ Hg—Cl \end{matrix} + 2NH_3 = Hg\begin{matrix} NH_2 \\ Cl \end{matrix} + NH_4Cl$$

Mercurous chloride absorbs dry ammonia gas forming $Hg_2Cl_2.2NH_3$ Mercurous chloride occurs native in Spain and some other countries The mineral is called *horn quicksilver*. Both mercurous and mercuric chlorides are employed in medicine

The vapour density of mercurous chloride —The vapour density of mercurous chloride at 518° is 235 5 ($O_2 = 32$) This number agrees with 235 5 required for the simple molecule HgCl If mercury be a dyad, and if it has a constant unchangeable valency, the formula should be Hg_2Cl_2, that is, Cl—Hg—Hg—Cl. In that case, the observed vapour density means that the mercurous chloride dissociates into mercuric chloride and mercury $Hg_2Cl_2 = Hg + HgCl_2$, the theoretical vapour density of which is $\frac{1}{2}(200 + 270 9) = 235 5$, the same as for HgCl The vapour

density determination does not therefore furnish a definite answer to the obvious question The vapour of calomel forms an amalgam with gold when a piece of gold leaf is suspended in the vapour, owing to the presence of mercury vapour. It is possible that gold leaf decomposes calomel vapour, and, at best, the experiment only shows that *some* dissociation occurs, whereas the observed density requires *complete* dissociation The argument based on the constant valency of mercury is of little value Hence an *experimentum crucis*—that is, an experiment which will decide the question without ambiguity—is still wanting The best arguments in favour of the dissociation hypothesis ($Hg_2Cl_2 \rightleftharpoons HgCl_2 + Hg$) are due (1) to H B Baker He claims that the vapour density of calomel, perfectly dry, corresponds with the formula Hg_2Cl_2, but if the calomel be not so completely dried, it is probable that Hg_2Cl_2 dissociates into Hg and $HgCl_2$, analogous with the behaviour of perfectly dried ammonium chloride, which is known to behave in this manner (2) Smith and Menzies—see p 301.

Cupric chloride, $CuCl_2$.—This salt can be made by dissolving the metal in a mixture of nitric and hydrochloric acids, as well as by the usual methods burning the metal in chlorine, etc Cupric chloride, when anhydrous, is a dark brown solid Free chlorine can be detected in the vapour of cupric chloride at 344° Cupric chloride dissolves in a small quantity of water forming a deep green solution which deposits rhombic crystals of $CuCl_2.2H_2O$ on evaporation If the aqueous solution of cupric chloride be diluted with a larger volume of water, the solution becomes blue and loses its green tint, the green tint is restored if the blue solution be concentrated by evaporation When ammonia gas is passed into an aqueous solution of cupric chloride, blue crystals of $CuCl_2.4NH_3.H_2O$ are deposited This compound loses all its water and half its ammonia when heated between 120°–125° When the anhydrous chloride is exposed to ammonia gas, a blue solid, $CuCl_2.6NH_3$ is formed. Both salts when heated give green $CuCl_2.2NH_3$, and at higher temperatures this compound decomposes into nitrogen, cuprous chloride, ammonia, and ammonium chloride $6(CuCl_2.2NH_3) = 6CuCl + 6NH_4Cl + 4NH_3 + N_2$. The constitution of the "metal-ammonia" compounds, called the "ammines," is discussed later.

Cuprous chloride, CuCl.—When a solution of cupric chloride in concentrated hydrochloric acid is digested with metallic copper, and the acid solution is poured into water, a white precipitate of cuprous chloride separates. When either cuprous or mercurous chloride is heated in a current of chlorine, the "-ic" salt is produced, *e g* $2CuCl + Cl_2 = 2CuCl_2$ and conversely, when either cupric or mercuric chloride is heated in a current of hydrogen, or brought in contact with nascent hydrogen, the "-ous" salt is produced, followed *immediately* by the reduction of the chloride to the metal Stannous chloride, $SnCl_2$, reduces mercuric to mercurous chloride, and the latter, in turn, to metallic mercury; sulphurous acid H_2SO_3, reduces cupric to cuprous chloride. Conversely cuprous chloride can be oxidized to cupric chloride by exposing the hydrochloric acid solution of cuprous chloride to the atmosphere The solution becomes brown and then deposits a greenish-blue solid, $CuCl_2.3CuO.4H_2O$, which appears to resemble the mineral *atacamite*. Cuprous chloride, dissolved in hydrochloric acid or in ammonia, readily absorbs carbon monoxide and acetylene Both solutions are employed in gas analysis for the removal of carbon monoxide from gaseous mixtures. The amount of gas absorbed

never exceeds the ratio Cu : CO, and it is probable that a compound $CuCl \cdot CO \cdot 2H_2O$ is formed. When a solution approaching saturation is brought in contact with a gas free from carbon monoxide, some carbon monoxide may leave the solution and contaminate the gas.

Silver chloride, AgCl.—Silver chloride occurs in nature as the mineral *horn silver*. Like mercurous chloride, silver chloride is formed when a soluble chloride is added to a solution of a silver salt. The white precipitate melts at about 490°, forming a yellow liquid which becomes darker the higher the temperature. The liquid solidifies on cooling to a tough horny mass. Silver chloride absorbs ammonia gas, forming $AgCl \cdot 2NH_3$, and $AgCl \cdot 3NH_3$, some properties of which will be discussed later. Silver chloride is soluble in concentrated hydrochloric acid, in alkaline chlorides, aqueous ammonia, potassium cyanide, and in sodium thiosulphate. Its solubility in water was indicated on p. 159. See also p. 274.

Action of light on silver chloride.—When silver chloride is exposed to light, it darkens, assumes a violet tint, which passes into brown, and finally turns black. It is probable that the chloride decomposes into free chlorine and silver subchloride, Ag_2Cl, thus: $4AgCl \rightleftharpoons 2Ag_2Cl + Cl_2$. The system is in equilibrium when the vapour pressure of the chlorine has reached a certain value. When the silver subchloride is exposed to the action of chlorine gas in darkness, silver chloride, AgCl, is formed. The amount of silver chloride decomposed, for equilibrium, depends upon the intensity of the light. If chlorine be removed from the sphere of the reaction, by, say, mixing the silver salt with a suitable organic compound which "binds" the chlorine, the reaction proceeds to an end. These properties of silver chloride are employed in photography. Silver bromide and silver iodide appear to behave in an analogous manner, but the bromide is generally considered most suitable for photographic purposes.

Photography.—A celluloid film or glass plate is coated on one side with a film of gelatine containing, say, silver bromide in suspension, and dried. The plate is placed in the camera, and *exposed* by focusing the image of the object to be photographed on to the plate for a moment. The silver bromide is affected in some way so that the most intense change occurs where the light is brightest, while the change is less intense in the shadows. No visible change is apparent until the plate is *developed*. The plate is developed by treating it with a reducing agent—ferrous sulphate, pyrogallol, or some special developer. The developer continues the change started by the light, but is without action on the unexposed parts of the plate. As a result, finely divided silver is deposited on the parts of the plate illuminated by the light reflected from the object. The deposit is thickest where the light was most intense. Hence, the dark parts of the object appear lightest on the plate, and the light parts dark. The image is thus the reverse of the object, and the plate is accordingly called a *negative*. The silver salt which has not been affected by the light nor by the developer is now removed, and the image thus *fixed* on the plate by immersing the plate in a solution of sodium thiosulphate. The plate is then washed and dried. A *print* is made by laying the negative upon sensitized paper—that is, paper prepared in a similar way to the negative—so that the light must pass through the negative before striking the paper. The negative absorbs the light in proportion to the thickness of the deposit of silver, so that the print has the same shading as the object. The paper is then treated with

a solution of sodium thiosulphate to fix the image. The print may be *toned* by immersing it in a solution of gold chloride so that some of the silver is replaced by gold, this gives the print a warm reddish tone, if a platinum salt be used instead of gold, a steel-grey tone is produced The image on the print will be the reverse of that on the negative, and will therefore correspond with the object Hence the print may be called the *positive*

Auric chloride, $AuCl_3$—If gold be dissolved in a mixture of hydrochloric and nitric acids (*aqua regia*), yellow needle-like crystals of a complex acid—**hydrochloroauric acid**, $HAuCl_4$—separate from moderately concentrated solutions If the solution be evaporated to dryness, and the residue dissolved in a little water, reddish crystals of $AuCl_3.2H_2O$ can be obtained by concentrating the solution These crystals lose water and give brown deliquescent crystals of the anhydrous chloride when heated to a low temperature Hydrochloroauric acid, $HAuCl_4$, forms a series of complex salts with the alkaline chlorides $NaAuCl_4.2H_2O$, etc These salts are called **chloroaurates** The monobasic radicle is "$AuCl_4$" The constitution of complex salts of this kind is discussed later

Aurous chloride, AuCl—When auric chloride is heated to 180° it passes into a yellowish-white powder which is aurous chloride Aurous chloride is decomposed by water into auric chloride and metallic gold $3AuCl = 2Au + AuCl_3$ If aurous oxide, Au_2O, be dissolved in hydrochloric acid, it forms auric chloride and metallic gold Both the gold chlorides are unstable, and decompose when heated above 180° into chlorine and the metal Gold is precipitated from its solutions of the chloride by reducing agents of all kinds—stannous chloride, ferrous sulphate, formic, sulphurous, and oxalic acid, etc

§ 10 Tin and Lead Chlorides

Stannic chloride, $SnCl_4$—This salt can be made by heating powdered tin with an excess of mercuric chloride, $2HgCl_2 + Sn = 2Hg + SnCl_4$, or by the following process

Place 60 grams of metallic tin in a flask, and heat it by placing a Bunsen's burner underneath When the tin is melted, pass a stream of dry chlorine, prepared as indicated above, so that the gas plays directly on the metal, Fig 107 When the metal in the flask has all disappeared, add some tinfoil to the liquid with the receiver, and close the receiver with a stopper After standing 12 hours so as to allow the dissolved chlorine to react with the tin, distil the product from a retort, and reject the first few drops of the distillate If the later distillate be coloured, repeat the treatment with tinfoil, etc, and collect the fraction which distils at 113 9°

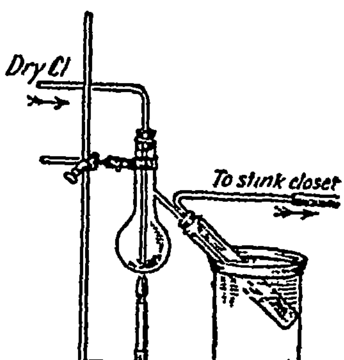


FIG 107 —Preparation of Stannic Chloride

Stannic chloride is a fuming colourless liquid which boils at 113 9°. It unites with water, forming a series of crystalline hydrates: $3H_2O$, $5H_2O$, and $8H_2O$ The pentahydrate $SnCl_4.5H_2O$ is used as a mordant[1]

[1] A mordant is a substance which can be precipitated in the fibre of a fabric to be dyed, and which then combines with the dye to form an insoluble compound

in dyeing under the name "oxymuriate of tin" (Aqueous solutions of stannic chloride are not stable owing to hydrolysis $SnCl_4 + 4H_2O \rightleftharpoons 4HCl + Sn(OH)_4$) Stannic chloride forms a series of complex salts potassium chlorostannate, $SnCl_4.2KCl$, or K_2SnCl_6, in which the radicle "$SnCl_6$" is bivalent The liquid was known to A Libavius in 1605, and was called *spiritus fumans Libavii*

Stannous chloride, $SnCl_2$.—Dissolve metallic tin in hydrochloric acid, and evaporate the solution until monoclinic crystals, $SnCl_2.2H_2O$, separate This hydrate loses its water and forms anhydrous stannous chloride when dried *in vacuo* The anhydrous salt is also made by heating metallic tin in a stream of hydrogen chloride, and by heating a mixture of metallic tin with mercuric chloride $HgCl_2 + Sn = SnCl_2 + Hg$ The mercury volatilizes and leaves a residue of stannous chloride Stannous chloride is soluble in a small amount of water, the addition of an excess of water or exposure to the air leads to the precipitation of a basic chloride $2SnCl_2 + 2H_2O = SnCl_2.SnO.H_2O + 2HCl$ The formula of stannous oxychloride is variously represented $SnCl_2SnO.H_2O$, $Sn_2OCl_2.H_2O$, $SnO.HCl$, $Sn(OH)Cl$ (Stannous chloride is a powerful reducing agent, and readily combines with oxygen or with chlorine When solutions of stannous chloride are exposed to the air, oxygen is absorbed, and stannous oxychloride and stannic chloride are formed $6SnCl_2 + O_2 + 2H_2O = 4Sn(OH)Cl + 2SnCl_4$ Stannous chloride boils at 606° The vapour density of stannic chloride, above 900°, corresponds with $SnCl_2+Cl_2$, and at lower temperatures with the mixture $SnCl_4 \rightleftharpoons SnCl_2+Cl_2$ Stannous chloride also combines with iodine, forming $SnCl_2I_2$, and it is used for titrating iodine in volumetric analysis

Lead chloride, $PbCl_2$.—This salt separates as a white curdy precipitate when hydrochloric acid or a soluble chloride is added to a solution of a lead salt (It is also made by dissolving lead oxide or carbonate in hot hydrochloric acid) On cooling, the solution deposits crystals of lead chloride, $PbCl_2$ The salt is generally said to be fairly soluble in hot water, and sparingly soluble in cold water 100 grams of water at 0° dissolve 0.67 gram of $PbCl_2$, at 50°, 1.70 gram, and at 100°, 3.34 grams When lead chloride is heated in air, lead oxychloride, Pb_2OCl_2, or $PbCl_2.PbO$, is formed By adding hot limewater to a boiling solution of lead chloride, $PbCl_2PbO.H_2O$, or $Pb(OH)Cl$, separates This compound is used as a white pigment under the commercial name "Pattinson's white lead," and the pigment "Cassel's yellow" is an oxychloride of lead, approximately $7PbO + PbCl_2$, made by heating lead oxide with ammonium chloride

Lead tetrachloride, $PbCl_4$.—This is an unstable chloride formed when chlorine is passed through hydrochloric acid in which lead chloride is suspended, or when lead dioxide is dissolved in concentrated hydrochloric acid The salt, $PbCl_4.2NH_4Cl$, or $(NH_4)_2PbCl_6$, is precipitated when ammonium chloride is added to the solution This salt ammonium chloroplumbate corresponds with ammonium chlorostannate If ammonium chloroplumbate be treated with concentrated sulphuric acid in the cold, a yellow oil, $PbCl_4$, is obtained This decomposes in contact with moisture, forming lead oxide and hydrogen chloride The tetrachloride is unstable, decomposing $PbCl_4 = PbCl_2 + Cl_2$ This compound is interesting because it shows that very probably lead can be quadri- as well as bi-valent.

§ 11. Iron, Aluminium, Chromium, Manganese, Cobalt, and Nickel Chlorides

Ferric chloride, $FeCl_3$.—The anhydrous chlorides of the metals can generally be made by the action of chlorine upon the metals, or by the action of chlorine, or the vapours of carbonyl chloride, or carbon tetrachloride upon the metallic oxides at a low red heat. The first-named operation can be conducted in the following manner:

A bundle of iron wire is placed in the middle of a hard glass tube *A*, Fig. 108. Connect one end of this tube with an apparatus for generating chlorine and two sulphuric acid wash bottles for drying the gas; connect the other end of the tube with a dry receiver, made from a wide-necked bottle, with a two holed stopper, and one tube leading to the stink closet as indicated in the diagram. Conduct a fairly rapid stream of chlorine through the tube, and when all the air has been expelled, gently warm the tube with a flame which does not touch the glass. In a short time, the iron and chlorine will react with brilliant sparks. The ferric chloride which is formed can be sublimed into the receiver by warming the neck, etc., with

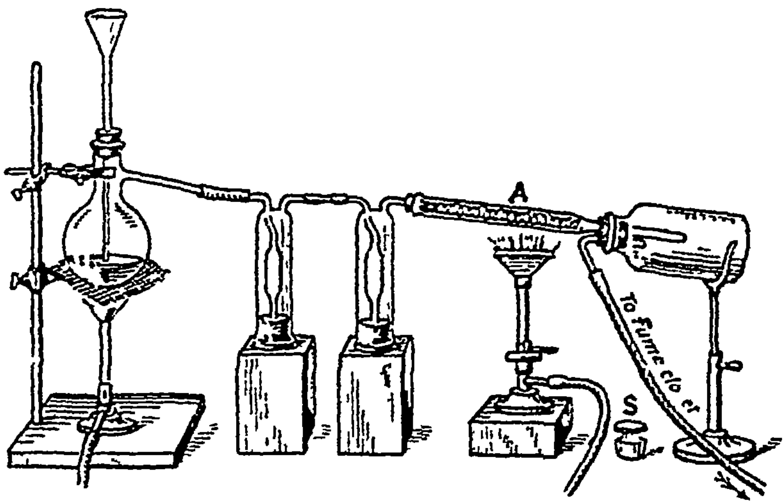


FIG. 108.—Preparation of Anhydrous Ferric Chloride.

a second large flame moving to and fro along the tube. When the iron is all converted into ferric chloride, shake the salt into a dry wide mouthed bottle. The bottle must be well-stoppered—stopper *S*, Fig. 108—because the salt is very hygroscopic or deliquescent.

Ferric chloride forms hexagonal crystals which appear greenish by reflected light, and dark red by transmitted light. Anhydrous ferric chloride dissolves in water with the evolution of much heat. When aqueous solutions are evaporated, crystals of $FeCl_3.6H_2O$ are formed as the solution cools, but the anhydrous salt cannot be obtained by the evaporation of aqueous solutions on account of hydrolysis. The hydrated salt can be obtained by dissolving iron, iron carbonate, or iron oxide in hydrochloric acid, and oxidizing the solution with a little nitric acid, or hydrogen peroxide. Hydrolysis occurs when aqueous solutions of ferric chloride are boiled or left standing some time. An insoluble oxychloride, or a soluble hydroxide and hydrochloric acid are formed. The two latter can be separated by dialysis.

Dialysis.—While studying the rate of diffusion of salts through membranes of parchment paper, Thomas Graham (1861) noticed that certain substances diffuse very slowly through the parchment. Gelatine and glue might be cited in illustration. The membrane is nearly impervious to these substances. Graham applied the term colloids—from the Greek κόλλα (kolla), glue—to those substances which diffuse but slowly through the parchment. On the other hand, substances like sodium chloride, magnesium sulphate pass through the membrane much more quickly. Crystalline salts are typical of those substances which diffuse rapidly, and hence Graham called them crystalloids. In illustration:

CRYSTALLOIDS	COLLOIDS
Potassium chloride	Albumen
Cane sugar	Gums
Magnesium sulphate	Starch
Hydrochloric acid	Gelatinous aluminium hydroxide
Sodium chloride	Gelatinous ferric hydroxide
Barium chloride	Gelatinous silicic acids

It must be added that a great many substances can exist in both the colloidal and crystalloid condition, so that it is better to distinguish between the colloidal and crystalline conditions of matter rather than between "crystalloids" and "colloids".[1] In modern chemistry the term "colloid" comprises much of what was formerly called "amorphous," although some so called colloids may after all be crystalline. It must not be supposed that the colloids do not pass through the parchment at all. Graham found that when the time of diffusion of hydrochloric acid—HCl—was taken as unity, the rate of diffusion of an equal quantity of sodium chloride was 2.3, cane sugar 7, egg albumen 49, and caramel 98. On account of these great differences, Graham proposed a useful method of separating colloids from crystalloid substances in solution. The crystalloid is removed by diffusion through a membrane of parchment, bladder, or some similar substance. The process is called dialysis—from the Greek διά (dia), through, λύω (lyo), I loosen. The operation will be understood from the following description.

FIG. 109.—Dialyzer.

A piece of parchment or bladder is bound across one end of a glass or gutta percha hoop so as to form a kind of shallow dish, Fig. 109, narrower at the base than the open top. A mixed solution of albumen (the white of an egg) and potassium chloride in water is poured into the "dish." This vessel is placed in another dish *B*, containing distilled water. The water in the outer vessel is renewed every few hours. The dish containing the mixed solution is covered by a clock glass to protect it from dust. In about three days, practically all the potassium chloride will have passed through the membrane into the outer vessel, while the egg albumen will remain in the inner compartment. The whole apparatus is called a dialyzer. See also Fig. 300.

If a few drops of ammonia be added to a solution of ferric chloride, a reddish brown precipitate of ferric hydroxide will be formed. This re dissolves in the unchanged ferric chloride. When the solution of ferric chloride is saturated with the ferric hydroxide, any further addition of ammonia will give a permanent precipitate of ferric hydroxide. Add a

[1] Wo. Ostwald (1911) advocates the term dispersoid system in place of "colloidal solution."

few drops of hydrochloric acid to dissolve the precipitated ferric hydroxide, and dilute the solution with water so that it contains about 5 per cent of solid in solution. Pour this solution into the dialyzer, the soluble ferric chloride and ammonium chloride pass into the outer vessel, and a dark red liquid, called "dialyzed iron," remains in the inner vessel If dialyzed iron be allowed to stand for some weeks in a glass vessel, it gelatinizes. Here, then, we have two kinds of colloids (*fluid* colloids are said to be in the sol condition, and *gelatinous* or pectinous colloids are said to be in the gel condition) When the solvent is water, the colloids are either hydrogels (gelatinous) or hydrosols (fluid), if alcohol be the solvent alcogels or alcosols etc The dialyzed iron is in the hydrosol condition

In an earlier chapter, solutions were defined to be "mixtures which appear clear and homogeneous in ordinary daylight, and which cannot be separated into their constituent parts by filtration through paper, and by decantation" It is now possible to apply Graham's dialysis test, and subdivide solutions[1] according as the substance in solution diffuses rapidly—crystalloid solutions, or slowly—colloidal solutions—through parchment paper To summarize

Solutions are clear and homogeneous in daylight

1 *Crystalloid solutions* are optically inert, and the dissolved matter diffuses rapidly through parchment

2 *Colloidal solutions* give an opalescence with Tyndall's test, they usually appear heterogeneous under the ultramicroscope, and the substance in solution diffuses very slowly through parchment

(*a*) *Sol* The fluid colloidal condition

(*b*) *Gel* The solid or gelatinous colloidal condition

It must be clearly understood that no hard and fast line of demarcation can be made between mere suspensions, colloidal and crystalloid solutions Perfect definitions are not yet possible

The vapour density of ferric chloride—Anhydrous ferric chloride boils about 280° At temperatures below 400°, the vapour density corresponds with Fe_2Cl_6, above that temperature the vapour density diminishes, until, at about 750°, the vapour density corresponds with the molecule $FeCl_3$, possibly also some dissociation,

$$Fe_2Cl_6 \rightleftharpoons 2FeCl_2 + Cl_2,$$

occurs, at any rate, free chlorine can be detected in the vapour at 122°–123° The vapour density curve at different temperatures is indicated in Fig 110

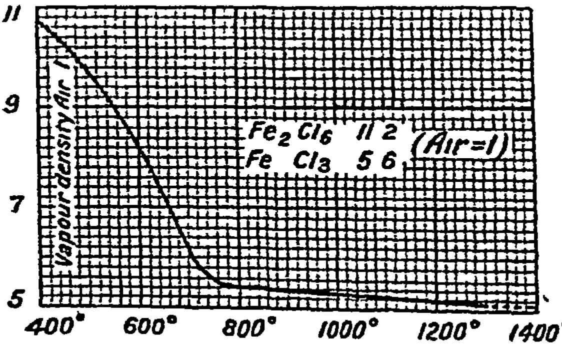


Fig 110—Vapour Density of Ferric Chloride

The hydrates of ferric chloride—The curve *AB*, Fig 111, represents the effect of additions of anhydrous ferric chloride on the freezing point of solutions of water The freezing point falls rapidly with the

[1] The criteria "homogeneous in daylight" and "speed of diffusion" are quite arbitrary The same remark applies to "filtration through paper," because colloidal solutions could be separated into their constituents if *a compact enough* filtering medium—say, more or less vitreous unglazed earthenware—were employed.

separation of ice from the solution until the eutectic point B at $-55°$ is attained, and the solution contains 2 75 molecules of Fe_2Cl_6 per 100 molecules of the solvent. At the eutectic point, the whole solution freezes *en masse*. The solid is a mixture of ice and $Fe_2Cl_6\ 12H_2O$ Any further addition of ferric chloride raises the temperature at which solid separates from the solution, and the solid which separates is the dodekahydrate, $Fe_2Cl_6\ 12H_2O$, alone The curve BC thus represents the solubility of the dodekahydrate in water This salt continues to separate until a temperature of 37° is attained The solution is then nothing but fused

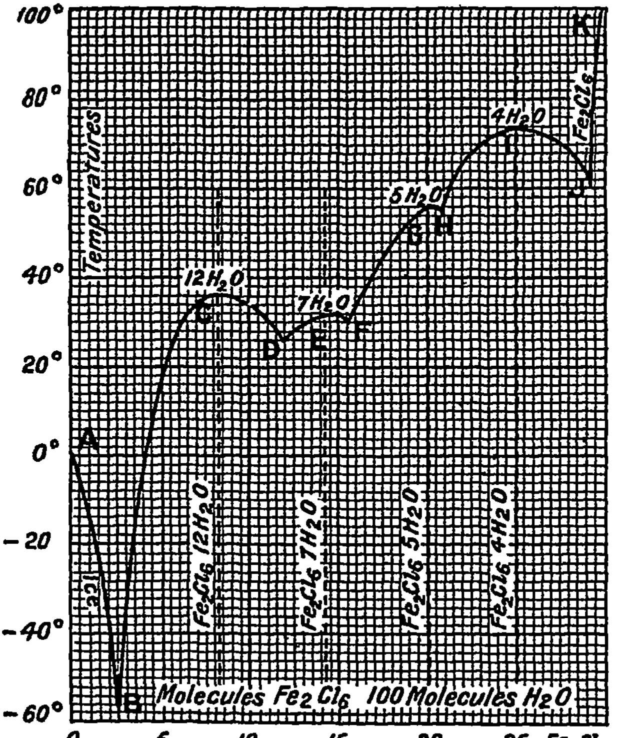


FIG 111 —Freezing Points of the Hydrates of Ferric Chloride

$Fe_2Cl_6\ 12H_2O$ This hydrate melts at 37° Any further addition of ferric chloride to the solution depresses the temperature at which solid dodekahydrate separates until a second eutectic D is reached at 27 4° The solution then solidifies *en masse*. The eutectic solid is a mixture of the dodekahydrate and the heptahydrate $Fe_2Cl_6\ 7H_2O$ By adding more salt, the temperature of solidification is raised, and the heptahydrate separates from the solution This continues until a temperature of 32 5° is attained, when the solution is virtually fused heptahydrate $Fe_2Cl_6\ 7H_2O$ Any further addition of ferric chloride depresses the temperature at which the heptahydrate separates until a third eutectic is attained The eutectic mixture of heptahydrate and pentahydrate solidify *en bloc* at 30° The remainder of the curve can be followed in the same manner until the anhydrous ferric chloride is obtained

It will be observed that if a solution of ferric chloride be evaporated between 30° and 40°, the solution will solidify below 37°, when $Fe_2Cl_6\ 12H_2O$ is formed as more water is driven off, the mass will liquefy when the eutectic D melting at 27 4° is produced, solidification occurs when the heptahydrate $Fe_2Cl_6\ 7H_2O$ melting at 32 5° is formed, and the solution

will liquefy at 70° when it has the composition corresponding with the eutectic *F*. The solution will again solidify as the pentahydrate: $Fe_2Cl_6.5H_2O$ melting at 56° appears. Similar phenomena recur with the tetrahydrate, $Fe_2Cl_6.4H_2O$

If we confine the attention for a moment, to the curve between the points *A* and *C*, it will be apparent that we have the typical curve indicated in Fig 111, and the same statement applies to the portions *CDE*, *EFG*, *GHI* and *IJK*. The point *C* represents a fused solution of $Fe_2Cl_6.12H_2O$: and the point *E* a fused solution of $Fe_2Cl_6.7H_2O$ The point *D* corresponds with the eutectic mixture of both the dodeka- and the heptahydrate. Each maximum point—*C*, *E*, *G*, and *I*—corresponds with a definite hydrate: and each minimum—*B*, *D* *F*, *H*, *J*—with the eutectic mixture of the two compounds represented by the adjacent maxima The solubility curve of ferric chloride thus reveals the presence of four stable hydrates, namely $Fe_2Cl_6.12H_2O$; and $Fe_2Cl_6.7H_2O$, $Fe_2Cl_6.5H_2O$, and $Fe_2Cl_6.4H_2O$

Ferrous chloride, $FeCl_2$.—Heat metallic iron in a stream of dry hydrogen chloride in a similar apparatus to that employed for the preparation of ferric chloride. Fig. 108 White feathery crystals of anhydrous ferrous chloride are produced. These are very deliquescent. The aqueous solution of ferric chloride, or the salt formed by dissolving iron, or ferrous carbonate in hydrochloric acid deposits pale bluish-green crystals of $FeCl_2.4H_2O$. When heated in air ferrous chloride forms ferric oxide and ferric chloride $12FeCl_2 + 3O_2 = 2Fe_2O_3 + 8FeCl_3$. Between 1200° and 1300° in an atmosphere of hydrogen chloride the vapour density corresponds with $FeCl_2$, and at lower temperatures possibly Fe_2Cl_4

Aluminium chloride $AlCl_3$.—The aqueous solution made by dissolving the metal in hydrochloric acid deposits crystals of $AlCl_3.6H_2O$ These crystals decompose when heated, forming alumina, etc. : $2(AlCl_3.6H_2O) = 6HCl + 9H_2O + Al_2O_3$ The crystalline hydrate cannot be prepared by the evaporation of the aqueous solution unless in a stream of hydrogen chloride, because of hydrolysis (see magnesium chloride) Anhydrous aluminium chloride is made on a large scale by passing chlorine over a mixture of carbon and alumina at a high temperature. The volatile product is condensed in a receiver to which no moisture has access. Neither the chlorine nor the carbon can alone react with the oxide under the conditions of the experiment. The joint action of the carbon and chlorine is needed for the work: $Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO$.

Anhydrous aluminium chloride can also be prepared either by heating aluminium turnings in a current of dry chlorine; or in a rapid stream of dry hydrogen chloride gas, in the apparatus illustrated in Fig 108 The aluminium turnings should be cleaned free from grease by washing with alcohol and ether, and finally drying at 150° When all the air has been expelled from the apparatus by the stream of hydrogen chloride, heat the bulb containing the aluminium. The metal reacts with the gas $2Al + 6HCl = 2AlCl_3 + 3H_2$. The aluminium chloride passes into the receiver It may be necessary to heat the tube leading into the receiver from time to time to prevent the blocking of the tube by the condensation of aluminium chloride

Anhydrous aluminium chloride sublimes without fusion at 183°, forming white hexagonal crystals. If heated under pressure, aluminium chloride melts before volatilization. The anhydrous chloride fumes strongly in moist air: $AlCl_3 + 3H_2O = Al(OH)_3 + 3HCl$. The heat

of solution of anhydrous chloride is $Al_2Cl_6 + Aq = Al_2Cl_6aq + 153.7$ Cals., and the corresponding value for ferric chloride, Fe_2Cl_6, is $+ 63.4$ Cals. The vapour density at about 200° corresponds with Al_2Cl_6, and above 450° with $AlCl_3$. (Aluminium chloride forms double salts with ammonia, phosphorus pentachloride, alkaline chlorides, etc. The salt $AlCl_3.3NaCl$ was used by Deville for the preparation of metallic aluminium.)

Manganous chloride, $MnCl_2$.—This salt is prepared by dissolving the oxide or carbonate in hydrochloric acid, and evaporating the solution. Rose red or pink monoclinic crystals of $MnCl_2.4H_2O$ are obtained. The anhydrous salt is made by heating the crystals in a stream of hydrogen chloride. Manganous chloride forms double salts with the alkaline chlorides. The vapour density between 1200° and 1500° corresponds with the formula, $MnCl_2$.

Manganic chloride.—A cold solution of manganese dioxide in concentrated hydrochloric acid behaves as if it contained a higher chloride than $MnCl_2$. The solution probably contains a large proportion of $MnCl_3$; some think $MnCl_4$ is also present. Manganese trichloride, $MnCl_3$, is made by treating manganese dioxide, suspended in carbon tetrachloride, with dry hydrogen chloride. The precipitated solid is a mixture of manganese tri- and tetra-chlorides, which is decomposed by water; but when the mass is extracted with anhydrous ether, and the ether evaporated, manganese trichloride remains as a black powder with a greenish tinge. It is immediately hydrolyzed by water. The residue from the ether extraction is manganese tetrachloride, $MnCl_4$, which is soluble in absolute alcohol. The alcoholic solution slowly decomposes. The rapid decomposition of these chlorides in aqueous solution explains the hypothetical character of our statements about the higher chlorides of manganese until a solvent was discovered in which they could be dissolved without rapid decomposition. The isomorphism of the following pairs of salts: $MnCl_3.2NH_4Cl.H_2O$ with $FeCl_3.2NH_4Cl.H_2O$; and of $FeCl_3.2KCl.H_2O$ with $MnCl_3.2KCl.H_2O$, indicates a certain analogy between iron and manganese.

Chromic chloride, $CrCl_3$.—The anhydrous salt and the hydrate $CrCl_3.6H_2O$ are prepared by methods similar to those employed for aluminium chloride. Free chlorine can be detected in the vapour of chromic chloride at 355°. A number of different hydrates have been made by dissolving chromic hydroxide in hydrochloric acid, or by reducing the chromates and dichromates in solutions of hydrochloric acid. There are three varieties of the hexahydrated chloride: monoclinic crystals of a violet colour—the β salt—made by passing hydrogen chloride into a saturated solution of the oxide in hydrochloric acid at a low temperature 8° to 10°; at a higher temperature, the violet solution becomes green, and when saturated with hydrogen chloride, it deposits rhombic green crystals—the α salt. Another green salt—the γ salt—is obtained by treating the mother liquid from the violet crystals with ether saturated with hydrogen chloride. These three salts are remarkable in that when freshly prepared solutions are treated with silver nitrate with the α salt one third the total chlorine is precipitated as silver chloride; with the γ salt two thirds; and with the violet β salt all is precipitated. This is symbolized by Werner's formula to be described later:

$[Cr(H_2O)_4Cl_2]Cl.2H_2O$	$[Cr(H_2O)_5Cl]Cl_2.H_2O$	$[Cr(H_2O)_6]Cl_3$
Green α salt	Green γ salt	Violet β-salt

The violet crystals of the hexahydrate are practically insoluble in water unless a trace of chromous chloride, $CrCl_2$, or certain other reducing agents, be present

Chromous chloride, $CrCl_2$—When chromic chloride is heated in a current of hydrogen, a white crystalline compound, $CrCl_2$, is formed The crystals dissolve in water forming a blue solution which rapidly absorbs oxygen and forms the green chromic chloride A solution of chromous chloride is formed by dissolving the metal in hot hydrochloric acid The green solution is reduced to the blue solution of chromous chloride by the action of zinc

Cobaltous chloride, $CoCl_2$—The hydrated salt—$CoCl_2 6H_2O$—crystallizes from solutions of the oxide or carbonate in hydrochloric acid in the form of ruby-red monoclinic crystals which are easily soluble in water The crystals at about 100° form the monohydrate, $CoCl_2 H_2O$, and at about 120°, the anhydrous chloride $CoCl_2$ The latter gives reddish solutions when dissolved in water

Nickelous chloride, $NiCl_2$—Anhydrous nickel chloride, $NiCl_2$, is formed in a similar manner to the cobalt salt The golden-yellow crystals of anhydrous salt dissolve slowly in water The aqueous solution deposits green monoclinic prismatic crystals, $NiCl_2 6H_2O$, which are inclined to effloresce in air.

Questions

1 Describe the preparation of chlorine and hydrogen chloride and contrast their properties What is the relative density of the two substances?—*Aberdeen Univ*

2 Write a short essay on *one* of the following subjects (*a*) Catalysis and catalytic agents, (*b*) The chemical work of Priestley and Lavoisier, (*c*) The determination of the atomic weight of chlorine —*Aberystwyth Univ*

3 Mention four elements that will liberate hydrogen from hydrochloric acid, and write equations of reactions —*Sheffield Scientific School, U S A*

4 State the law of combination of gases by volume and Avogadro's hypothesis From a consideration of the combination of gaseous hydrogen and chlorine how can it be shown that the molecule of hydrogen consists of parts? —*Univ North Wales*

5 What would be the cost of materials in preparing a 20 per cent solution of hydrochloric acid if 1 kilo of sodium chloride costs 2*d*, 1 kilo of 90 per cent sulphuric acid costs 3*d* and a kilo of Glauber's salt, $Na_2SO_4 10H_2O$, can be sold for 1½*d* per kilo?—*F Rudorff, Grundriss der Chemie*

6 What kinds of salts hydrolyze in water? Give three equations illustrating hydrolysis —*Sheffield Scientific School, U S A*

7 What is meant by the dissociation of a gas? How is dissociation distinguished from ordinary decomposition? Discuss the dissociation phenomena exhibited by hydrogen peroxide under the influence of heat —*Sheffield Univ*

8 Describe the preparation of zinc chloride from zinc oxide Calculate the volume of a solution of hydrochloric acid, density 1 1 and containing 20 per cent by weight of acid required to make 50 grams of this salt —*Sheffield Scientific School, U S A*

9 Describe fully how you would prepare (*a*) a solution of hydrogen chloride (*b*) a solution of chlorine from common salt How could it be shown that the solution of the acid is free from chlorine?—*Univ North Wales*

10 How did Faraday effect the liquefaction of chlorine? Give a short sketch of recent researches upon the liquefaction of gases —*London Univ*

11 What discoveries are associated with the names of Priestley, Davy, Faraday, Graham?—*Aberdeen Univ*

12 Write the formulæ you are accustomed to use for the chlorides of potassium, silver, aluminium, tin, mercury, and iron which of these expressions may be regarded as representing molecular composition, and upon what grounds may they be so regarded?—*London Univ*

CHAPTER XIV

THE RELATIONS OF CHLORINE—IODINE, BROMINE, AND FLUORINE

§ 1 Bromine

Atomic weight, Br = 79 92 ; molecular weight, Br_2 = 159 84 , valency, 1 , 3 , 5 7 valent , melting point, −7 3° , boiling point, 59° Specific gravity of the liquid at 0°, 3 1883 Vapour density (H_2 = 2), 158 85 , (air = 1), 5 524

History —While studying the mother liquid which remains after the crystallization of salt from the water of the salt marshes of Montpellier, A J Balard (1826) was attracted by the intense yellow coloration developed when chlorine water is added to the liquid. Balard digested the yellow liquid with ether , decanted off the supernatant ethereal solution , and treated this with potassium hydroxide The colour was destroyed. The solution was evaporated to dryness The residue resembled potassium chloride, and when heated with manganese dioxide and sulphuric acid furnished red fumes which condensed to a dark brown liquid with an unpleasant smell [1] Balard called this substance " muride," but afterwards changed the name to " bromine "—from the Greek *βρῶμος* (bromos), stench Balard demonstrated the elementary nature of bromine, and showed its relation to iodine and chlorine

Occurrence —Bromine does not occur free in nature Small quantities occur combined in many silver ores , and it occurs associated with potassium, sodium, magnesium, or calcium in many mineral waters, salt springs, and sea water The water of the Atlantic is said to contain 0 007 per cent of magnesium bromide , the water of the Dead Sea, 9 per cent. , the mineral water of Ohio, from 3 4 to 3 9 per cent of magnesium bromide Bromine is also found in marine animals and plants, in rock salt, etc The saline deposits of Stassfurt contain about one per cent of magnesium bromide From this latter source, the main supply of the bromine in commerce is derived

Manufacture —The mother liquid remaining after the separation of the potassium salts, p 228, contains about 0 25 per cent of bromine in the

[1] J von Liebig used to relate that some years before Balard's discovery he received, from a salt manufactory in Germany, a vessel containing bromine, or at least a product very rich in bromine, with a request to examine it Believing the liquid to be iodine chloride, he did not subject the specimen to a very exhaustive study When he heard of the discovery of Balard, Liebig saw his mistake, and placed the vessel in a special cabinet for storing mistakes—*l'armoire des fautes* Liebig pointed this out to his friends to show how easily one could get very close to a discovery of the first rank and yet fail to grasp the facts when guided by preconceived ideas.

form of magnesium bromide The hot liquid is allowed to percolate down a tower packed with earthenware balls, here the descending liquid meets an ascending stream of chlorine gas The magnesium bromide is decomposed $MgBr_2 + Cl_2 = MgCl_2 + Br_2$ The bromine vapours leave the top of the tower through an exit pipe, and are liquefied in a suitable condenser In the electrolytic process, the mother liquid is electrolyzed The magnesium bromide can be decomposed by the electric current before the magnesium chloride, and thus it is possible and practicable to separate the bromine

Purification.—The bromine is purified by redistillation The chlorine is removed by distillation from calcium or ferrous bromide or by collecting separately in a receiver the first 1 to 4 per cent of the distillate in the form of a volatile compound or mixture of chlorine and bromine If anhydrous bromine be needed, it must be redistilled off concentrated sulphuric acid. If iodine be present, this must be removed by treatment with a copper salt Cuprous iodide CuI is precipitated

Properties.—At ordinary temperatures, bromine is a heavy mobile reddish-brown liquid—specific gravity at 0°, 3 1883 It freezes to a yellowish-brown crystalline mass at −7°, and boils in air at 59° It is very volatile, and gives off a dark reddish-brown vapour at ordinary temperatures Bromine separates in the form carmine-red needle-like crystals, when a solution of bromine in carbon disulphide is cooled to −90° The solid is almost colourless at −252° Bromine has a disagreeable irritating smell, and it attacks the eyes as well as the mucous membrane of the throat and nose It is poisonous, and attacks the skin producing troublesome sores 100 grams of water dissolve 4 3 grams of bromine at 0°, and 3 2 grams at 20° Bromine is also soluble in chloroform, carbon disulphide, alcohol, ether, and acetic acid When bromine water is cooled to 0°, it forms a hydrate, $Br_2.10H_2O$ Bromine resembles chlorine in general chemical properties, but is not quite so energetic It forms bromides analogous with chlorides, and only unites slowly with hydrogen in sunlight

Atomic and molecular weights.—Analyses of silver bromide show that the experimental value of the combining weight of bromine is very close to 79 92 when silver is 107 88 This number, 79 92, also represents the atomic weight of bromine, because it represents the smallest amount of bromine in any one of the known volatile compounds of bromine

At about 100° the vapour density is 5 87 (air = 1), and at 228°, 5 52 This corresponds with the molecule Br_2. At 1570° the vapour density is but two-thirds of its value at 228°, showing that the molecule is probably dissociating into atoms.

Uses.—Bromine is used in metallurgy, photography, and the chemical industries. It is also used as a disinfectant, for which purpose it is sold under the name "bromum solidificatum," which is kieselguhr—a siliceous earth—saturated with bromine. Bromine is also used as an oxidizing agent.

§ 2 Hydrogen Bromide—Hydrobromic Acid

Molecular weight, HBr = 80 93 Melting point, −88 1°, boiling point, −67 1°. Vapour density (H_2 = 2), 80 23, (air = 1) 2 79 One litre of the gas under normal conditions weighs 3 608 grams, specific gravity of liquid, 1 63 at 10°

Hydrogen bromide.—This gas can be obtained directly from its elements If a stream of hydrogen be bubbled through warm bromine, the hydrogen

which passes along is highly charged with bromine vapour, and when ignited, dense clouds of hydrogen bromide are formed If a mixture of hydrogen and bromine be passed through a red hot tube containing platinized asbestos, or a hot platinum spiral, the elements rapidly combine The platinum acts as a stimulant or catalytic agent An apparatus for this experiment is illustrated in Fig 112 The hydrogen is dried by passage through concentrated sulphuric acid in the wash-bottle *A*; and bromine is placed in the bulb *B* When all the air is expelled from the apparatus, the bromine is warmed slightly, and the mixed gases are passed through the tube *C* containing platinized asbestos Any bromine which escapes uncombined is absorbed by red phosphorus, slightly damped, which is packed along with glass wool in the tower *D*, here any free bromine forms a phosphorus bromide If the hydrogen bromide is to be absorbed by water, the products of the reaction—a mixture of hydrogen and hydrogen bromide—are passed through an empty wash bottle *E*, and then through

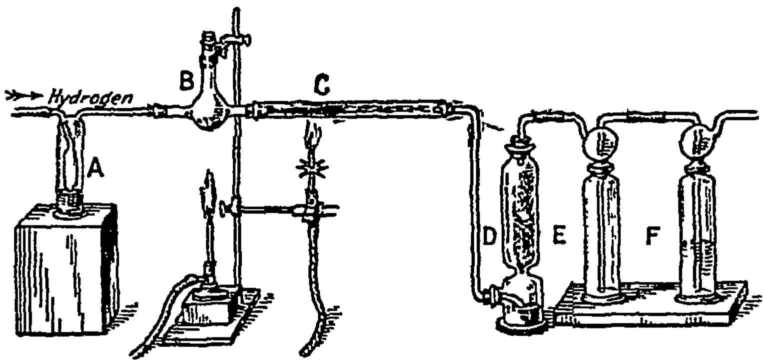


FIG 112—Catalytic Process for Hydrogen Bromide.

a similar wash-bottle half filled with water The empty wash bottle *E* is reversed so that there is no danger of water passing beyond the bottle if back suction occurs Hydrogen bromide is also formed when some of the metallic bromides are reduced to metals in a current of hydrogen Thus, at a red heat with silver bromide $2AgBr + H_2 = 2HBr + 2Ag$ Hydrogen bromide is sometimes made by the action of bromine on hydrocarbons—*e g* naphthalene, $C_{10}H_8$, benzene, C_6H_6, anthracene, $C_{10}H_{10}$, etc —but the gas is then more or less contaminated with organic products.

The following is the method usually employed in the laboratory Mix, say, 10 grams of red phosphorus with 80 grams of fine sand, and place the dry mixture in a dry distillation flask, *A*, Fig 113 Add about 20 c c of water Close the flask with a rubber stopper fitted with a tap funnel *B*, and delivery tube as indicated in Fig 113 The end of the tap funnel is drawn to a fine point Connect the delivery tube with a tower or a U tube *C* containing glass wool and slightly damp red phosphorus The gas may be collected by the upward displacement of air, or absorbed in water as illustrated in the previous diagram, or collected over mercury, *E* In the latter case, a safety funnel may be attached to the delivery tube at *D*, so that variations of pressure inside the apparatus may be rapidly adjusted without risk of explosion and back suction of mercury About 60 grams of bromine are placed in the tap funnel, and allowed to fall, drop by drop, on the red phosphorus As each drop of bromine comes in contact with the phosphorus,

a flash of light is produced Some prefer to keep the flask immersed in cold water during the early stages of the reaction, and to wrap a towel round the flask in case of an explosion The heat of the reaction volatilizes some bromine which is retained by the phosphorus in the U-tube, when all the bromine has been run into the flask, a further quantity of hydrogen bromide may be obtained by gently warming the flask The hydrogen bromide can be dried by means of a tube packed with calcium bromide

The chemical reactions which occur during the preparation of hydrogen bromide by the action of bromine on phosphorus and water, are probably somewhat as follows Phosphorus tri- and penta-bromide are first formed, these react with the water $PBr_3 + 3H_2O = H_3PO_3 + 3HBr$, and $PBr_5 + 4H_2O = H_3PO_4 + 5HBr$ The whole reaction is usually represented on the supposition that phosphorus tri-bromide is formed $2P + 6H_2O + 3Br_2 = 2H_3PO_3 + 6HBr$ If too little water be present, some crystals of phosphonium bromide—PH_4Br—may be formed in the flask owing to the decomposition of the hot phosphorous acid, H_3PO_3, thus · $4H_3PO_3 = 3H_3PO_4 + PH_3$, and $PH_3 + HBr = PH_4Br$

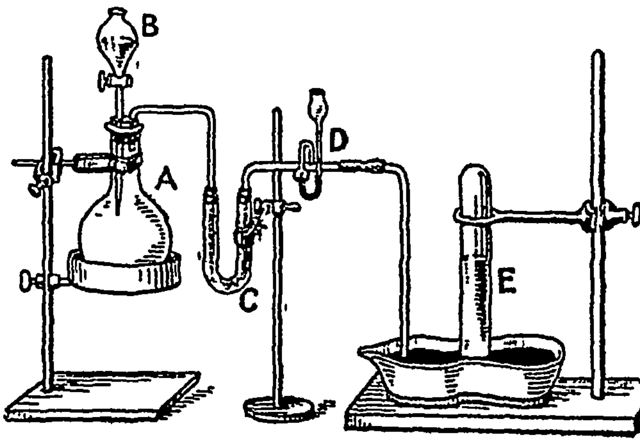


FIG 113 —Preparation of Hydrogen Bromide

Hydrobromic acid —It is convenient to call the gas "hydrogen bromide," and aqueous solutions "hydrobromic acid" Hydrobromic acid is formed when hydrogen sulphide is passed into bromine covered with a layer of water $H_2S + Br_2 = 2HBr + S$ If sulphur dioxide be used in place of hydrogen sulphide a pale yellow homogeneous liquid is obtained $SO_2 + Br_2 + 2H_2O \rightleftharpoons 2HBr + H_2SO_4$ When this liquid is distilled in, say, the apparatus depicted in Fig 114, an aqueous solution of hydrogen bromide is obtained The reaction is reversible, sulphuric acid is reduced by hydrogen bromide forming bromine and sulphur dioxide. This helps us to understand why hydrogen bromide cannot be satisfactorily prepared by the action of sulphuric acid upon potassium bromide as in the preparation of hydrogen chloride by the action of sulphuric acid upon potassium chloride When the attempt is made, colourless hydrogen bromide is first given off, but the issuing gas immediately acquires a yellow colour, and then a brown tinge, showing that bromine in also evolved. The issuing gas also contains sulphur dioxide Hence not only does the reaction $KBr + H_2SO_4 = KHSO_4 + HBr$ take place, but also the consecutive reaction $2HBr + H_2SO_4 = SO_2 + Br_2 + 2H_2O$, and the method is accordingly impracticable If dilute sulphuric acid be employed with the idea of preventing an appreciable decomposition of the hydrogen bromide, the amount of hydrogen bromide obtained is very small If phosphoric acid be used in place of sulphuric

acid because phosphoric acid does not deoxidize so readily as sulphuric acid, the action—$KBr + H_3PO_4 = KH_2PO_4 + HBr$—is rather low

Properties —Hydrogen bromide is a colourless gas with a strong penetrating smell. It fumes in air It condenses to a liquid at −73°, and solidifies to a colourless solid at −87° The gas is very soluble in water A solution saturated at 0° has a specific gravity 1 78, and the hydrogen bromide and water are approximately in the proportion HBr H_2O 100 grams of water at 0° dissolve 221 grams of hydrogen bromide, and 199 grams at 20° The acid containing 48 per cent of hydrogen bromide distils unchanged in composition, weaker acids lose much water until the constant boiling acid is obtained, which distils at 126° and 760 mm. pressure, more concentrated acids lose hydrogen bromide until the constant boiling acid is obtained Two crystalline hydrates — HBr H_2O and HBr $2H_2O$—have been made.

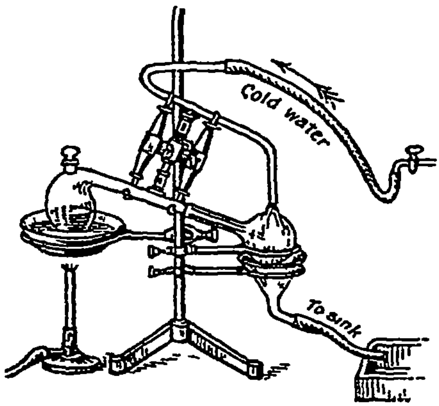


FIG 114 —Distillation of Hydrobromic Acid

Dry hydrogen bromide has no action on litmus Hydrogen bromide resembles hydrogen chloride very closely in chemical properties, but hydrogen bromide is less energetic Hydrobromic acid forms bromides in the same way that hydrochloric acid forms chlorides Hydrogen bromide is more easily decomposed than hydrogen chloride At 800° decomposition is quite appreciable The gas is also slightly decomposed by exposure to sunlight. The composition of hydrogen bromide has been determined in a similar manner to that of hydrogen chloride

§ 3 Iodine

Atomic weight, I = 126 92 molecular weight, I_2 = 253 84 valency 1 3 5, 7-valent Melting point 116 1° boiling point 184 35° Specific gravity of the solid, 4 933 Vapour density, 253 84 (H_2 = 2), and 8 72 (air = 1)

History —In 1812, B Courtois, a manufacturer of saltpetre, near Paris, used an aqueous extract of varec or kelp [1] for decomposing the calcium nitrate from the nitre beds, as indicated later on Courtois noticed that the copper vats in which the nitrate was decomposed were rapidly corroded by the liquid, and he traced the effect to a reaction between the copper and an unknown substance in the lye obtained by extracting the varec or kelp with water On evaporating the aqueous extract of the kelp crystals of potassium sulphate first separate, then follow crystals of sodium sulphate,

[1] During the stormy months of spring, seaweeds are washed on to the western coasts of Ireland Scotland and France The inhabitants collect the weed and burn it in large heaps at as low a temperature as possible The ash thus obtained is called *kelp* in Scotland and *varec* in Normandy.

sodium chloride, and afterwards sodium carbonate. The remaining liquid is heated with sulphuric acid in a retort. "A vapour of a superb violet colour" is obtained which condenses in the tube of the retort and in the receiver in the form of brilliant crystalline plates. Courtois communicated his discovery to Clément and Désormes, who published some results of their study of this new substance in 1813. A year later Gay-Lussac published an extensive and remarkable memoir on this new substance which was called iodine—from the Greek ἰοειδής (ioeidēs), violet. Gay-Lussac established the elementary nature of iodine, and demonstrated its relationship to chlorine. About the same time, H. Davy confirmed many of Gay-Lussac's results.

Occurrence.—Varec or kelp contains from 0.1 to 0.3 per cent. of iodine. The kelp derived from deep seas is richer in iodine than kelp from shallower parts. Iodine also occurs in small quantities in sea water; sea plants; sea animals; in some land plants and animals; in codliver oil; in the thyroid gland of animals; and in many mineral springs. It occurs combined with silver in some Mexican ores, and in some South American lead ores. Most of the iodine of commerce is extracted from the mother liquid remaining after the separation of sodium nitrate from caliche in Peru, etc. Caliche contains about 0.2 per cent. of iodine, and the mother liquid after the extraction of the sodium nitrate, contains 5 to 20 per cent. of sodium iodate.

Manufacture.—The mother liquid remaining after the crystallization of the sodium nitrate from the aqueous extract of caliche is treated with sodium bisulphite, which first reduces the sodium iodate to sodium iodide, and finally to free iodine: $2NaIO_3 + 5NaHSO_3 = 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2$. The solid iodine which separates is allowed to settle, washed, and pressed into blocks. The impure iodine so obtained is sublimed in iron retorts and the vapours condensed in a series of earthenware receivers.

Iodine is extracted from the ash of seaweed by concentrating the aqueous extract so as to remove alkaline carbonates, chlorides, and sulphates by crystallization. The mother liquid containing the iodides and some bromides is treated first with sulphuric or hydrochloric acid, and then with manganese dioxide. On heating the mixture, iodine is liberated: $2NaI + Cl_2 = 2NaCl + I_2$. This is condensed in earthenware receivers arranged so that any water distilled over is condensed and drained off. A ton of kelp is said to furnish 10 to 12 lbs. of iodine.

Purification.—Commercial iodine always contains both chlorine and bromine in solid solution. To purify the iodine, dissolve resublimed iodine in a concentrated solution of potassium iodide; and precipitate the iodine from the solution by adding an excess of water. Wash and dry the solid. The dry precipitate is then intimately mixed with potassium iodide and heated in, say, a beaker covered with a glass flask kept cold by a current of water. A crust of the purified iodine condenses on the bottom, outside the cooled flask. Pure iodine has also been obtained by heating cuprous iodide to about 240° in a current of dry air.

Properties.—At ordinary temperatures, iodine is a dark bluish-black crystalline solid. The rhombic crystalline plates have a metallic lustre, and a specific gravity of 4.933 at 4°. Iodine vaporizes slowly at ordinary

temperatures, and it has a slight smell resembling chlorine It is very sparingly soluble in water 100 c c of a saturated solution at 25° contain about 0 32 gram of iodine, and is coloured a faint brown The iodine is much more soluble if potassium iodide be also present. Iodine is fairly soluble in many organic solvents—alcohol, ether, acetone, chloroform, carbon disulphide, benzene, etc. The colours of the solutions differ with different solvents hydrocarbons, chloroform, and carbon disulphide give violet solutions, while alcohol, water, aqueous solutions of potassium iodide, and ether give brown solutions This is illustrated by the following experiment Place a layer of carbon disulphide, *A*, at the bottom of a glass cylinder, Fig 115, on this a layer of water, *B*, and above all, a layer of ether, *C* Drop some crystals of iodine into the cylinder The lowest layer will form a violet solution, water will give a yellowish-brown solution, and the ether a brown solution Many of the violet coloured solutions become brown when cooled to low temperatures, and conversely, many brown solutions become violet when heated It is probable that free iodine is present in the violet solutions, and that the brown coloration is due to the formation of a compound of iodine with the solvent In brown solutions of iodine in potassium iodide, for example, the iodine is supposed to form an unstable potassium tri-iodide, KI_3—$KI + I_2 \rightleftharpoons KI_3$ This salt has indeed been isolated in the form of dark coloured needle shaped crystals. It is probable that in this salt the potassium is univalent, and the iodine uni- and tervalent, $K{-}I{=}I_2$. In the salts $RbICl_4$, CsI_3, etc, the iodine appears to be quinquevalent A great number of polyiodides and polybromides of the univalent cæsium and rubidium have been prepared, they crystallize well, and are more stable than the corresponding potassium salts *e g* $CsBr_5$, CsI_3, RbI_3 $RbBr_3$ $RbICl_4$, CsI_3, NH_4I_3, etc

FIG 115 — Colours of Iodine Solutions

Iodine resembles chlorine and bromine in its chemical properties, but it is rather less energetic Chlorine can displace bromine from bromides, and both chlorine and bromine can displace iodine from iodides. Chlorine can displace bromine from bromates, and iodine can displace chlorine from chlorates $2KClO_3 + I_2 = 2KIO_3 + Cl_2$ Iodine, like chlorine and bromine, combines with many elements, forming iodides When phosphorus and iodine are placed in contact, the phosphorus melts and inflames, forming either phosphorus triodide, PI_3, or phosphorus pentaiodide, PI_5 Antimony powder inflames spontaneously when it is shaken with iodine vapour, iodine and mercury also combine energetically when heated.

When in contact with starch, iodine forms an intense blue coloration The reaction is delicate enough to reveal the presence of 0 0000001 grm of iodine per c c The blue colour disappears when heated to about 80°, but returns on cooling The "blued" starch is supposed to be either a solid solution of iodine in the starch, or else an "addition" compound of iodine with starch

Uses —Iodine is used in medicine, the manufacture of dyes and organic compounds, in photography, and in analytical chemistry

Atomic and molecular weight —The combining weight of iodine, determined from the analysis of silver iodide and other iodine compounds,

ranges from 126·79 to 126·93, and the best representative value is supposed to be 126·92 when oxygen is 16. This is the smallest amount of iodine in all known volatile compounds containing iodine, and hence this number is taken to be the atomic weight of iodine. This agrees with a two atom molecule, for the vapour density of iodine, at 600°, is 8·7 (air = 1), or 125·9 (H = 1). The lowering of the freezing point and the raising of the boiling point of solutions of iodine in carbon disulphide acetic acid and chloroform show that the molecular weight is nearly 254, corresponding with I_2.

When iodine vapour is heated above 700° its density diminishes steadily up to about 1700°, when it becomes constant at half its value at the lower temperature. Thus the theoretical density for I_2 is 8·78, and for I, 4·39.

Temperature	480°	855°	1043°	1275°	1390°	1468°
Vapour density	8·74	8·07	7·01	5·82	5·27	5·06
Dissociation	0	8·6	25·0	50·5	66·2	73·1 per cent

Without doubt, the iodine molecule, I_2, dissociates into atoms $I_2 = I + I$. Related phenomena will be discussed later.

§ 4 Equilibrium, and the Kinetic Theory of Chemical Action.

When a mixture of equal volumes of iodine and hydrogen gases is passed through a red hot tube, or, better, over finely divided platinum, or platinized asbestos, Fig. 112, or charcoal, some hydrogen iodide, HI, is formed. If hydrogen iodide gas be treated in a similar way, some iodine and hydrogen are produced. In either case, if the temperature of the tube be 440°, we have approximately 80 per cent. of hydrogen iodide, and 20 per cent. of a mixture of equal volumes of iodine and hydrogen. The only apparent effect of the catalytic agent—platinized asbestos, etc.—is to accelerate the reaction, and if these agents be absent, the time required to make 80 per cent. of hydrogen iodide from the mixture of hydrogen and iodine is much longer. Once this proportion of hydrogen iodide has been formed, the composition of the exit gases remains unchanged, however long the mixture may be heated at 440°, with or without the catalytic agents.

Bimolecular reactions.—We may now extend our previous study of opposing reactions. In the bimolecular reaction

$$A + B \rightleftharpoons M + N$$

let C_A and C_B respectively denote the concentrations of the substances A and B, expressed in gram-molecules per litre. Similarly, let C_M and C_N respectively denote the concentrations of M and N. We have previously found that the speed of the reaction is equal to the product of the affinity or force driving the reaction, k, and the concentrations of the reacting substances, that is, the velocity of the reaction A + B is equal to kC_AC_B. If A and B are the same, so that we have $2A \rightleftharpoons M + N$, the speed of the $\rightarrow$ reaction at any instant will be represented by kC_A^2. When hydrogen iodide dissociates, we have $2HI \rightleftharpoons H_2 + I_2$. The speed of the $\rightarrow$ reaction at any instant will be represented by kC_{HI}^2, and the speed of the $\leftarrow$

reaction by $k'C_IC_H$ When equilibrium occurs, the speeds of these two reactions are the same, and therefore we have the condition of equilibrium

$$kC_{HI}^2 = k'C_HC_I \text{ or } \frac{k}{k'} = \frac{C_HC_I}{C_{HI}^2} = K$$

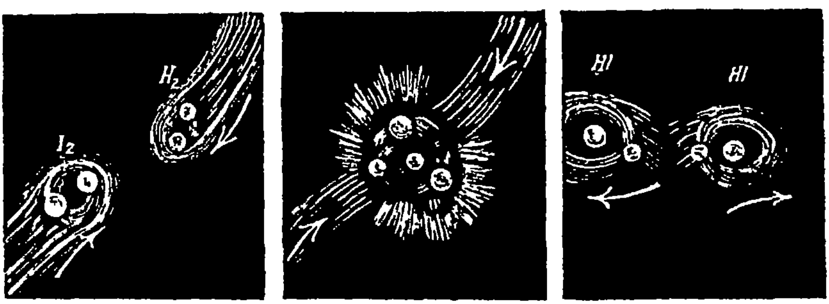
At 440°, when the system is in equilibrium, nearly 20 per cent of the hydrogen iodide will have dissociated Hence

$$(80 \text{ per cent }) \; 2HI \overset{440^\circ}{\rightleftharpoons} H_2 + I_2 \; (20 \text{ per cent })$$

This means that if 100 molecules of hydrogen iodide be heated to 440° in a closed tube, 20 will have dissociated when the system is in equilibrium Hence $C_{HI} = 80$, $C_{HI}^2 = 6400$, and $C_I = C_H = 10$. Hence

$$\frac{k}{k'} = \frac{1}{64} \text{ or } C_{HI}^2 = 64C_HC_I$$

This means that at 440°, when the concentration of the hydrogen and iodine is unity, these gases will combine 64 times as fast as hydrogen iodide of unit concentration will dissociate, p 97 It will be observed that



Molecules approach Molecules collide and react New molecules separate

FIG 116 —Imaginary Representations of the Reaction $I_2 + H_2 = 2HI$ according to the Kinetic Theory

each of the direct and reverse reactions is a bimolecular reaction because two molecules are involved in each reaction

The kinetic theory of chemical action —The kinetic theory gives an interesting view of chemical action Imagine a vessel filled with a mixture of equal volumes of iodine and hydrogen gases. The molecules of hydrogen and iodine must be continually crashing together *A certain proportion* of these collisions will result in chemical change In the earlier stages of the reaction, the number of collisions per second between the hydrogen and iodine molecules will be relatively great, but later, as the hydrogen iodide accumulates, the number of collisions between the hydrogen and iodine molecules will become fewer and fewer, and accordingly, the speed of formation of hydrogen iodide will become less and less Following a plan first used by G Martin, Fig 116 may be employed to illustrate a chemically fruitful collision between a hydrogen and an iodine molecule

Similarly, when two hydrogen iodide molecules crash together, a *certain proportion* of the collisions will result in a dissociation, so that an iodine

and a hydrogen molecule will result At first, the number of collisions will be few and far between, but, as hydrogen iodide accumulates in the system, the number of collisions between these molecules will increase Finally, when the number of chemically fruitful collisions per *second* between the iodine and hydrogen molecules is equal to the number of chemically fruitful collisions between the hydrogen iodide molecules, the system will subsequently undergo no perceptible change Obviously, this does not mean that chemical action has ceased Every time the proper molecules collide, hydrogen iodide will be formed or dissociated Both changes proceed with the same velocity, and consequently the composition of the gas as a whole does not alter As previously emphasized, equilibrium is not a state of tranquillity and repose Equilibrium is dynamic and active, not static and passive

Dissociation and combination are partial and incomplete.—As the temperature rises the average velocity of the molecules of a gas becomes greater and greater Although the *average* velocity of the molecules of a gas is constant at any temperature, the velocities of *individual* molecules must vary considerably because of collisions, etc It is possible that collisions between the *faster moving molecules* of hydrogen iodide, alone, result in dissociation $2HI = I_2 + H_2$, and that collisions between the slower moving molecules of hydrogen iodide do not produce dissociation, similarly, it may be that collisions between the *slower moving molecules* of hydrogen and iodine alone result in the formation of hydrogen iodide, and collisions between the fastest molecules do not lead to chemical action. Hence we can see how but a "certain proportion" of the collisions are chemically fruitful This view of the reaction leads to several other interesting inferences, but since direct proof of the fundamental hypothesis is wanting, sufficient has been given to indicate the trend of modern thought

The action of stimulants—contact action.—The speed of dissociation of hydrogen iodide at 518° is augmented threefold by raising the pressure from 0 5 to 2 atmospheres The tremendous condensation of gases on the surfaces of such substances as platinized asbestos, platinum black, charcoal, etc, shows that gases near the surfaces of these substances must be very very concentrated. E Mitscherlich (1843) estimated that gaseous carbon dioxide condensed on wood charcoal in layers about 0 005 mm thick, and the gaseous layer is nearly as dense as liquid carbon dioxide Hence it follows that the concentration of the molecules of one or both the reacting gases must be very great near the surface of the catalytic agent, and accordingly, the total number of collisions, and the number of chemically fruitful collisions in unit time will be augmented This means that the speeds of formation and dissociation of hydrogen iodide will be stimulated in the presence of such substances as platinized asbestos, etc In other words, these substances act as catalytic agents

A catalytic agent can alter the speed of a chemical action, but it cannot alter the condition of equilibrium.—Although the speed of a chemical reaction is modified by the presence of a catalytic agent, the final state of equilibrium is not affected If otherwise, we could allow these substances to react alternately with and without the catalytic agent, this would involve a change in the quantity combined, and the energy thus obtained could be made to do work This would lead to perpetual motion, which is assumed to be impossible, p 110. This deduction

has been confirmed experimentally with hydrogen iodide with and without platinum black.

Unimolecular reactions.—The last example is instructive. The state of the system in equilibrium will be represented by $kC_{I_2} = k'C_I^2$. If x denotes the proportion of iodine dissociated, and v the volume of the iodine vapour, then, since v volumes of iodine vapour becomes $2v$ volumes of dissociated iodine vapour, it follows that the concentration of the dissociated iodine will be x/v, and of the undissociated iodine $(1 - x)/v$. Hence for equilibrium

$$k\frac{1-x}{v} = k'\left(\frac{x}{v}\right)^2 \text{ or } K = \frac{k}{k'} = \frac{x^2}{(1-x)v}$$

In every gram-molecule of iodine (I_2) at 1043°, 0·25 gram molecule will be dissociated; hence, $x^2 = 0·0625$; $1 - x = 0·75$; and $K = 0·0833/v$. To evaluate v, remember that one gram molecule of iodine vapour at 0° and 760 mm. occupies 22·3 litres; and at 1043°, 107·5 litres. This quantity of gas contains 0·25 more molecules of iodine because of dissociation, and hence its volume is 107·5 + ¼ of 107·5 = 134·4 litres. Hence $K = 0·0833 \div 134·4 = 0·00062$, or $k : k' = 0·00062 : 1$, or $1 : 1600$ (nearly). Otherwise expressed, $C_{I_2} = 1600\, C_I^2$, that is, the atoms of iodine will unite 1600 times as fast as the molecules dissociate under such conditions that unit concentration of each is present, p. 268. The dissociation of iodine molecule is a unimolecular reaction because one molecule is concerned in the reaction; and the formation of the two atom molecule by the union of two one atom molecules is a bimolecular reaction because two molecules are concerned in the process.

We have just seen that according to the kinetic theory, the average velocity of the molecules becomes greater and greater as the temperature rises; and that although the *average* velocity is constant at any particular temperature, the velocities of *individual* molecules must vary considerably because of collisions, etc. The velocities of the faster moving molecules may finally become so great that the crash, on collision, displaces the atoms from their position of equilibrium in the molecules. Rise of temperature not only accelerates the movements of translation of the molecules themselves, but it also increases the velocities of the cyclic motions of the atoms within the molecule. The atomic movements may become so violent that the atoms of one or both molecules are thrown out of the sphere of one another's attraction when the swifter molecules collide. In other words, the molecules may be dissociated. The dissociation of the whole gas is only partial, because the faster moving molecules break down first. When the one atom iodine molecules collide, they enter the sphere of one another's attraction, and, if the velocities of the colliding molecules be not too great, the atoms remain in contact reforming a two atom molecule. As before, when the speeds of dissociation and re combination are equal, the system is in equilibrium.

The relative frequency of uni- and bi-molecular reactions.—Uni and bi molecular reactions are very much more frequent than more complex reactions involving three or more molecules. The number of *binary* collisions per second must be very much greater than the number of simultaneous collisions between, say, *three* molecules. When several molecules are involved in a reaction, the reaction must therefore be (1)

extremely slow, or (2) one or more intermediate reactions are involved—one molecule, for instance, may unite with another molecule and the pair (intermediate compound) later collides and reacts with a third molecule (see "consecutive reactions"), or (3) the reaction takes place in the vicinity of a boundary layer where the reacting molecules form a dense layer and are comparatively close together (see "contact action," above).

§ 5. The Effect of Temperature on Equilibrium—The Principle of Reversibility

The proportion of hydrogen iodide dissociated *decreases* with rise of temperature so long as the temperature does not exceed about 320°, above that critical temperature, the higher the temperature, the *greater* the amount of hydrogen iodide dissociated. This is illustrated by the graph, Fig 117 The thermal value of the reaction changes sign at about the same critical temperature, for instance, at 18°, the union of hydrogen and iodine is an *endothermal* reaction $H_2 + I_2 = 2HI - 6.1$ Cals, and at 520°, *exothermal* $H_2 + I_2 = 2HI + 4.4$ Cals Experience shows that a rise of temperature always favours endothermal reactions, and opposes exothermal reactions. *When a system is in physical or chemical equilibrium, a rise of temperature promotes the formation of those products which are formed with an absorption of heat, a rise of temperature resists the formation of those products formed with an evolution of heat, and a change of temperature has no effect on the equilibrium of reactions thermally neutral*—J H van't Hoff's equilibrium law (1884)

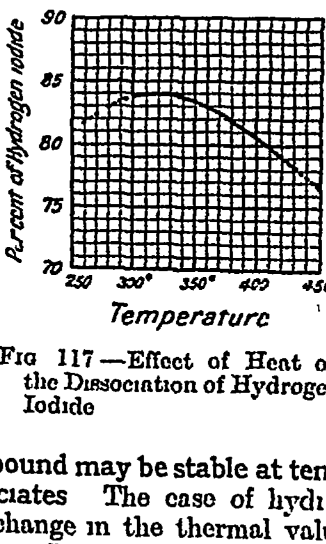


Fig 117—Effect of Heat on the Dissociation of Hydrogen Iodide

Some examples of this law have been previously indicated The law is simply a special case of the great principle of reversibility If an exothermal reaction becomes endothermal at a high temperature, we have the curious paradox discussed previously A compound may be stable at temperatures exceeding that at which it dissociates The case of hydrogen iodide is particularly instructive The change in the thermal value of the reaction corresponds with a change in the effect of a rise of temperature on the equilibrium The principle applies to physical equilibria When anhydrous sodium sulphate is dissolved in water, heat is evolved, and its solubility is diminished with a rise of temperatures, hydrated sodium sulphate dissolves in water with an absorption of heat, and its solubility increases with rise of temperature The vaporization of water is an endothermal reaction, and hence a rise of temperature favours vaporization, for it increases the concentration of the vapour phase

The effect of pressure on equilibria —The principle is also applicable with other forms of energy Thus *when a system is in a state of physical or chemical equilibrium, an increase of pressure favours the system formed with a decrease in volume, a reduction of pressure favours the system formed with an increase in volume, and a change of pressure has no effect on a system formed without a change in volume*—G Robin's law (1879) Thus

hydrogen iodide is formed from hydrogen and iodine without a change in volume, and the state of equilibrium is not affected by variations of pressure When ice melts, the liquid occupies a smaller volume than an equivalent amount of ice, experiment shows that the melting point of ice is lowered by pressure in agreement with the law With sulphur the converse is true The melting point of sulphur is raised by pressure, but the liquid phase has a greater specific volume than the solid phase

The principle is of wide application It says that natural changes take place in such a way that the existing state of things suffers the least possible change This has been called "the principle of the opposition of reactions to further change," or, *if a system in physical or chemical equilibrium be subjected to a stress involving a change of temperature, pressure, concentration, etc, the state of the system will automatically tend to alter so as to undo the effect of the stress*—H le Chatelier's law (1888) For instance, if the temperature of a system in equilibrium be raised a few degrees, the state of the system will change so as to induce the formation of that component or phase which absorbs most heat, and accordingly tend to lower the temperature If the $\rightarrow$ reaction be exothermal, the change will proceed in the reverse direction, and if the $\rightarrow$ reaction be endothermal, the system will change in the same direction Again, if the pressure of the dissociating iodine

$$\underbrace{I_2}_{1\ \text{vol}} = \underbrace{2I}_{2\ \text{vols}}$$

be increased, the state of the system will change so that the volume is diminished, and conversely, if the pressure be reduced, the state of the system will change so that the volume is increased, that is, the less the pressure the greater the amount of iodine dissociated. In the case of solutions, an increase of concentration will induce the formation of that component or phase which will lower the concentration of the solute added, and an increase of vapour pressure will lead to the formation of that component or phase which will reduce the vapour pressure, etc

§ 6 Hydrogen Iodide—Hydriodic Acid

Molecular weight, HI = 127 93 Melting point, −50 8°, boiling point, −34 1° Vapour density ($H_2 = 2$), 127 67, (air = 1) 4 44 Specific gravity of liquid, 2 27 at 12°

Hydrogen iodide —As in the case of the corresponding bromine compound, hydrogen iodide can be made by the direct combination of iodine and hydrogen It can be made by the action of iodine, on certain organic compounds—colophonium (resin), copaiva oil, etc. It is also formed by the action of hydrogen on silver iodide It cannot be made satisfactorily by the action of sulphuric acid upon potassium iodide Phosphoric acid, in place of sulphuric acid, gives very fair results Gaseous hydrogen iodide is usually made by the decomposition of phosphorus iodide by the action of water This is done by mixing red phosphorus and iodine in a dry flask, and gradually adding water from a dropping funnel to the products of the reaction This is a modification of the process employed for the preparation of hydrogen bromide rendered necessary, because bromine is liquid, and iodine solid Free iodine is removed from the gas by passing the hydrogen iodide through a tower of red phosphorus, and

the gas can be dried by passing it through a tube containing calcium iodide Hydrogen iodide cannot be collected over mercury because the mercury is attacked, it is usually collected by the upward displacement of air

Hydriodic acid —The term "hydrogen iodide" is reserved for the gas, and hydriodic acid for the aqueous solution An aqueous solution of hydrogen iodide can be made by the following process

Add about 3 grams of powdered iodine to 250 c c of water in a 500 c c flask and pass a stream of hydrogen sulphide slowly into the mixture In a few minutes all the iodine will have dissolved owing to the reaction $H_2S + I_2 = S + 2HI$ Add more powdered iodine, and continue the passage of the gas Repeat the operations until about 20 grams of iodine have been added Transfer 30 grams more iodine—50 grams in all—to the flask In about half an hour the iodine will all have dissolved in the hydrogen iodide already formed Continue passing hydrogen sulphide until the brown colour of the solution disappears, showing that all the iodine has been transformed into hydrogen iodide Pass a rapid stream of carbon dioxide or hydrogen through the warm solution to drive off the hydrogen sulphide Shake the solution to coagulate the sulphur, and remove the sulphur from the solution by filtration through glass wool The solution can be further purified by distillation, collect the fraction which boils between 125° and 130° This solution contains about 50 per cent of hydrogen iodide A more concentrated solution can be made by passing gaseous hydrogen iodide into cold water, or, better, into a solution of hydrogen iodide made as just described

Properties —Hydrogen iodide is a colourless gas which fumes strongly in air It condenses to a colourless liquid at 0° under 4 atmospheres pressure This boils at −34 14°, and freezes to a white solid which melts at −50 8° The gas is very soluble in water one volume of water at 10° dissolves about 425 volumes of hydrogen iodide The solution fumes strongly in air, and it has acid properties The aqueous solution, containing 57 per cent of hydrogen iodide, boils at 127° (774 mm), and distils unchanged in composition, weaker acids become stronger, and stronger acids become weaker on boiling until the 57 per cent acid is obtained, when the solution distils unchanged in composition Hydriodic acid is colourless when freshly prepared, but the solution soon turns brown owing to the oxidation of the hydrogen iodide $4HI + O_2 = 2H_2O + 2I_2$, and the dissolution of the separated iodine Gaseous hydrogen iodide is also decomposed when mixed with hydrogen and exposed to light The easy reduction of hydrogen iodide $2HI = I_2 + H_2$ corresponds with the energetic reducing qualities of this acid It is largely used as a reducing agent in organic chemistry

The composition of hydrogen iodide can be determined as indicated for hydrogen bromide The vapour density is 251 8 ($H_2 = 2$), and the formula HI

§ 7 Iodides and Bromides.

Hydriodic acid resembles hydrobromic and hydrochloric acids, and forms salts—iodides The chlorides likewise resemble the iodides and bromides, and they all can be prepared by similar processes Most metallic iodides when heated furnish the metal or a metallic oxide and liberate free iodine The iodides are usually less volatile than the corresponding chlorides and bromides Many iodides have characteristic colours

Potassium iodide, KI —This salt, as well as potassium bromide, KBr, and potassium chloride, can be prepared by similar methods, namely, by

the action of the corresponding acids upon the hydroxides or carbonates, by the action of the elements on solutions of the hydroxide followed by evaporation to dryness and subsequent ignition to decompose the oxysalts. The iodide is prepared by the following process (using bromine in place of iodine if the bromide is wanted)

Add 25 grams of iodine in small quantities at a time to a mixture of 50 c c of water with 7 grams of iron, turning in a flask with constant agitation Warm the mixture until the iodine has formed a yellow solution of ferrous iodide, FeI_2. Decant off the clear solution and mix it with 5 grams more of iodine in order to convert the ferrous salt to ferric iodide Warm the mixture until all the iodine is dissolved and pour it into a boiling solution of 17 grams of potassium carbonate in 50 c c of water The precipitate becomes flocculent after it has been heated for some time Test the clear solution to make sure that it is free from iron, if not, add more potassium carbonate to the boiling solution Evaporate the clear solution for cubic crystals of potassium iodide

Potassium iodide and bromide are readily soluble in water, and crystallize in cubes 100 c c of water dissolve 35 grams of potassium chloride, 65, potassium bromide, and 144, potassium iodide at 20° Potassium iodide and bromide are used in medicine and in photography

Silver iodide, AgI —This salt is formed by dissolving silver in concentrated hydriodic acid, or by treating silver nitrate with a soluble iodide Silver iodide is a yellow crystalline solid, it absorbs gaseous ammonia, forming a compound $2AgI \cdot NH_3$, which decomposes on exposure to air into ammonia and silver iodide Silver bromide, AgBr, is a pale yellow solid formed like the iodide with hydrobromic acid, etc It does not absorb gaseous ammonia like the chloride and iodide Silver bromide is decomposed by chlorine, and at 100° by hydrochloric acid. At ordinary temperatures, hydrobromic acid converts silver chloride into silver bromide The reaction is reversible $AgCl + HBr \rightleftharpoons AgBr + HCl$ When either silver bromide or silver chloride is treated with hydriodic acid, or potassium iodide, silver iodide is formed This is due to the fact that silver iodide is far less soluble than the other salts, and consequently separates from the sphere of the reaction The solubilities of these silver salts in water and in ammonia are as follows

TABLE XII —SOLUBILITIES OF SILVER SALTS

One litre	AgF grms	AgCl grms	AgBr grms	AgI grms
Water at 20°	1818	0 0016	0 000084	0 0000028
Ammonia, 5 per cent	—	2 3	0 114	—
Ammonia, 10 per cent	—	78 4	3 67	0·035

Silver bromide, like silver chloride, is very sensitive to light, and is largely used in dry plate photography

Cuprous iodide, CuI.—When aqueous solutions of potassium iodide and a copper salt are mixed together, it is possible that cupric iodide, CuI_2, is formed $CuSO_4 + 2KI = CuI_2 + K_2SO_4$, but the product is so unstable that it instantly decomposes into almost colourless cuprous iodide and iodine $2CuI_2 = 2CuI + I_2$ The beginning and end of the reaction are thus represented $2CuSO_4 + 4KI = 2CuI + I_2 + 2K_2SO_4$

This reaction is used in the determination of copper, and for separating iodine from chlorides and bromides, since the two latter salts do not give a cuprous salt under these conditions

Mercuric iodide, HgI_2 —When a solution of mercuric chloride, $HgCl_2$, is treated with a solution of potassium iodide, a yellow precipitate is obtained which changes in a few seconds to a scarlet colour The scarlet iodide is also made by rubbing 2 parts of mercury with 2 54 parts of iodine wetted with alcohol in a mortar Mercuric iodide is but sparingly soluble in water, but it is fairly soluble in alcohol and in nitric acid It readily dissolves in an excess of mercuric iodide, and in an excess of potassium iodide A solution of mercuric iodide in potassium iodide, made alkaline with potassium or sodium hydroxide, is called Nessler's solution. It gives a yellow or brown coloration in the presence of ammonia, according to the amount present This coloration is a delicate test for ammonia Mercuric iodide is dimorphous If the red tetragonal crystals be heated above 126°, they change into yellow rhombic crystals, which reform the original red iodide on cooling If the yellow iodide persists at ordinary temperatures, it rapidly changes to the scarlet iodide when rubbed with a glass rod

$$HgI_{2\,red} \overset{126^\circ}{\rightleftharpoons} HgI_{2\,yellow} \overset{223^\circ}{\rightleftharpoons} HgI_{2\,liquid}$$

Mercuric iodide melts at 223° to a red liquid, and a part sublimes, forming yellow rhombic needles Mercurous iodide, HgI, is formed when mercuric iodide or iodine is rubbed up with the right proportion of mercury in the presence of a little alcohol It is also formed when a soluble mercurous salt, say mercurous nitrate, is mixed with a solution of potassium iodide It is a greenish coloured powder slightly soluble in water The solution decomposes on standing, particularly if heated, forming mercury and mercuric iodide

§ 8 Calcium Fluoride

Calcium fluoride, fluorspar, or fluorite occurs in veins very frequently associated with lead ores, and sometimes by itself In the limestone caves of the Matlock district, Derbyshire, veins of fine crystals of this mineral are exposed In Derbyshire the mineral is called "blue john" or "Derbyshire spar" Fluorspar also occurs in many other districts The crystals belong to the cubic system, and the mineral occurs in cubes, octahedra, and related forms The crystals may be colourless, or tinted red, brown, yellow, green, blue, or violet by traces of contaminating metallic oxides, etc Some of the crystals are very pleasing, and such are used for ornamental purposes, jewellery, etc

Fragments of the crystals become luminous—fluorescent—when heated It has been proposed to mix this mineral with the carbon used for arc lighting so as to increase the luminosity of the arc light and decrease current consumption When heated to about 902°, fluorspar melts to an opaque greyish-white enamel. This property of fluorspar was mentioned by G A. Agricola in 1529, and he called the mineral "fluor lapis," literally "fluxing stone"—from the Latin *fluere*, to flow The German miners apply the term "spath" to all transparent or translucent minerals with a well marked cleavage, hence the German term for this mineral—

"Flussspath" Fluorspar is used as a flux in metallurgy, and in the manufacture of glass, enamels, and glazes

No gas is evolved when fluorspar is melted, but if fluorspar be strongly heated in an oxidizing flame, on charcoal, a pungent acrid smell, resembling hydrogen chloride, can be detected by bringing the nose near to the charcoal The fumes redden blue litmus, and if the residue be moistened with water and tested with red litmus, the paper will turn blue When fluorspar is mixed with sulphuric acid in a test-tube, no perceptible action occurs, but if the mixture be heated, a gas is given off and the glass is strongly corroded, showing that the gas developed by the action of hot sulphuric acid on fluorspar decomposes glass. The gas also attacks porcelain, zinc, copper, silver, etc, but it does not act very markedly upon lead, gold, platinum, wax, paraffin, and rubber The three latter will not stand heating, and consequently the further investigation of this gas—the "spirit of fluorspar"—hydrogen fluoride, must be conducted in lead, gold, or platinum vessels

§ 9 Hydrogen Fluoride—Hydrofluoric Acid

Molecular weight (over 90°) HF = 20 01 Melting point, −92 3°, boiling point, 19 4° Specific gravity of the liquid at 12 8°, 0 988 Vapour density (H_2 = 2) over 90°, 20 58

Manufacture of hydrofluoric acid—An aqueous solution of hydrofluoric acid is manufactured in the following manner The best quality of powdered fluorspar, free from silica, is gently heated to about 130° with concentrated sulphuric acid in a cast-iron pot with a cast-iron cover dipping into an annular trough and sealed with concentrated sulphuric acid The reaction is represented $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$ The cast iron retorts are provided with a series of leaden boxes as condensers These contain water or dilute hydrofluoric acid to absorb the gas from the retorts The condensers are submerged in water to keep them cool, and the acid so obtained is collected in leaden bottles Hydrofluoric acid is placed on the market in leaden, guttapercha, or wax (cerasine) bottles

Hydrogen fluoride—If potassium carbonate be neutralized with hydrofluoric acid, and then evaporated to dryness, potassium fluoride separates in cubic crystals readily soluble in water If the potassium fluoride be dissolved in hydrofluoric acid and evaporated, crystals of the double salt potassium hydrogen fluoride—KF HF—are obtained. This double salt is also called "acid potassium fluoride," "potassium bifluoride," and also Fremy's salt If this salt be dried by fusion in a platinum retort, and the platinum retort be then connected with a long platinum tube and platinum bottle immersed in a freezing mixture, the double fluoride decomposes when heated to redness $KHF_2 = KF + HF$, and the anhydrous hydrogen fluoride is condensed to a liquid. Anhydrous hydrogen fluoride can also be prepared by passing dry hydrogen over dry silver fluoride, and cooling the products of the reaction so as to condense the hydrogen fluoride to a liquid

Properties—Anhydrous hydrogen fluoride is a limpid liquid which fumes strongly in air It is very poisonous and dangerous to manipulate It forms ulcerated sores if a drop comes in contact with the skin J Nicklès, of Nancy, died in 1869 from accidentally breathing the vapour of this acid while trying to isolate fluorine The metals potassium and sodium dissolve in the pure acid, forming the corresponding fluorides and hydrogen The

liquid acid boils at 19.5°, and freezes at $-102.5°$. The crystals melt at -92.3. Hydrogen fluoride is very soluble in water, forming a corrosive liquid which readily dissolves many metals with evolution of hydrogen: $Fe + 2HF = FeF_2 + H_2$. Silver and copper also dissolve in the acid. If the acid be more concentrated than about 43 per cent. HF, it will become weaker on boiling; and if more dilute, the acid becomes stronger on boiling until an acid containing about 43 per cent. of HF, boiling at 111° (750 mm.), is formed. This distils unchanged in composition.

Etching glass.—Silicon burns in hydrogen fluoride, forming a gas, silicon fluoride SiF_4, and hydrogen. Hydrogen fluoride attacks quartz and siliceous substances, glass, etc., also forming silicon fluoride: $SiO_2 + 4HF = SiF_4 + 2H_2O$. Hydrofluoric acid is used in the analysis of silicates. When most silicates are repeatedly evaporated with hydrofluoric and sulphuric acids, all the silica is volatilized as silicon fluoride, etc., and the residue of sulphates can be examined by the standard methods. One of the most important properties of hydrofluoric acid is its etching action on glass. Glass may be etched with the gas or with an aqueous solution of the gas. In the former case, the etching appears opaque and dull; in the latter case, shining and transparent. For etching, the glass is covered with a film of wax, and the design to be etched on the glass is drawn on the waxed surface with a stylus; or else the parts of the glass not to be etched are coated with a resistant varnish. The surface is exposed to the action of the acid or gas, and very soon the glass is etched. The wax or varnish is then washed off with turpentine. The corrosive action of the hydrogen fluoride is due to the ready decomposition of the glass in contact with hydrogen fluoride. The silica forms silicon fluoride. The process is used for marking the scales on glass instruments.

Etching tests for fluorides.—In testing for fluorides, the substance under examination is warmed with sulphuric acid in a leaden vessel covered with a watch-glass. The watch-glass is coated with wax, and a design is scratched with a pin or knife, so as to expose the glass to the action of the acid. The wax is afterwards removed, and if the design is etched on the glass, fluorides were present.

Composition of hydrogen fluoride.—G. Gore (1870) measured the volume of hydrogen required to form hydrogen fluoride when heated with silver fluoride: $H_2 + 2AgF = 2HF + 2Ag$. He found that 100 volumes of hydrogen furnished 200 volumes of hydrogen fluoride, and hence inferred that hydrogen fluoride contains half its own volume of hydrogen, and half its own volume of fluorine. The formula is therefore H_nF_n. The vapour density at 100° corresponds with the molecule HF; the vapour density at lower temperatures than 80° shows that the molecule polymerizes.

Vapour density.—The vapour density of hydrogen fluoride at 21.4° ($H_2 = 2$) is 51.18 (or 1.773, air = 1); and it diminishes rapidly as the temperature rises, until, at 90°, it is 20.58. This is illustrated by the graph, Fig. 118. The lower number corresponds with a molecular weight HF. Hence, at 90°, hydrogen fluoride contains two *atoms*. At lower temperatures the molecule polymerizes to H_nF_n. There is, however, nothing to show what the molecules are. They *may* be partly HF, partly H_2F_2, H_3F_3, etc. The facts only permit the statement that below 90° gaseous hydrogen fluoride is a mixture of molecules H_mF_m, H_nF_n, . . . where the values of *m*, *n*, . . . are unknown. Similar results are obtained

by lowering the pressure, keeping the temperature constant, at, say, 32° The effect of hydrogen fluoride on the freezing point of water corresponds with the molecule H_2F_2.

Fluorides —The fluorides are made by the action of hydrofluoric acid on the metals, metallic oxides, hydroxides, carbonates, etc Most of the fluorides are soluble in water Silver fluoride, AgF, for instance, dissolves in about half its weight of water, and in this respect differs from the corresponding chloride, bromide, and iodide The solution of silver fluoride in water is alkaline to litmus, and hydrates $AgF\,H_2O$ or $AgF\,2H_2O$ separate as crystals when the solution is concentrated The fluorides of the alkaline earths—calcium, barium, and strontium—are very sparingly soluble, so also is yttrium fluoride The fluorides also usually unite with hydrogen fluoride, forming the so called acid fluorides, *e g* potassium hydrogen fluoride previously described. The graphic formula may be K—F—F—H, or K—F=F—H Similarly, the fluorides also unite with one another, forming double salts, *e.g* the double fluoride of aluminium and sodium, $AlF_3\,3NaF$ or cryolite The graphic formula for cryolite has been written

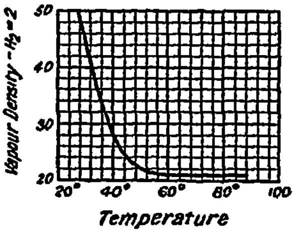


FIG 118 —Vapour Density of Hydrogen Fluoride

$$\text{Na—F—F—Al}<^{\text{F—F—Na}}_{\text{F—F—Na}} \quad \text{and also} \quad \text{Na—F}=\text{F—Al}<^{\text{F}=\text{F—Na}}_{\text{F}=\text{F—Na}}$$

where fluorine is supposed to be either bi- or ter-valent This curious property of fluorine is also illustrated by the polymerization of hydrogen fluoride at ordinary temperatures.

Aluminium fluoride, AlF_3 —The anhydrous fluoride is made by the action of gaseous hydrogen chloride upon a mixture of calcium fluoride and alumina heated white hot in a graphite tube The aluminium fluoride volatilizes, and calcium chloride remains behind $3CaF_2 + Al_2O_3 + 6HCl = 3H_2O + 3CaCl_2 + 2AlF_3$ It is also made by the action of silicon fluoride, SiF_4, upon alumina The crystalline hydrate, $2AlF_3\,7H_2O$, is made by dissolving alumina or the metal in aqueous hydrofluoric acid. As indicated above, aluminium fluoride combines with alkaline fluorides, forming double salts Thus, sodium aluminium fluoride, $AlF_3\,3NaF$, is made by digesting aluminium hydroxide, $Al(OH)_3$, with sodium fluoride The salt occurs native in South Greenland as a white, glassy, crystalline solid which resembles clouded ice in appearance, hence the name *cryolite*, literally "ice stone"—from the Greek *κρυος* (kryos), ice, *λιθος* (lithos), stone Cryolite melts at about 977°, and it is used as a flux It is also used in the manufacture of alum and aluminium salts, sodium salts, hydrofluoric acid, and the fluorides Cryolite is not now used as a source of aluminium metal

§ 10 Fluorine

Atomic weight, F = 19, molecular weight, F_2 = 38, uni or tri-valent Melting point, −233°, boiling point, −187°, vapour density (H_2 = 2), 37 7; (air = 1) 1 31, specific gravity of liquid 0 988 at 12 8°

Occurrence —Fluorine does not occur free in nature, but its com pounds are widely distributed, though not abundantly, in such minerals

as cryolite, fluorspar, etc. Small quantities occur in some of the micas, topaz, tourmaline, etc. Traces occur in sea-water, some mineral springs, bones, teeth, blood, milk, plants, etc.

History.—The fact that glass is attacked when exposed to the fumes produced when fluorspar is warmed with sulphuric acid was known to Schwankhard in 1670, and in 1771 K. W. Scheele stated that fluorspar is the calcium salt of "a peculiar acid":—fluoric acid. He prepared this acid by heating fluorspar with sulphuric acid in a tin retort. J. L. Gay-Lussac and J. Thénard (1807) prepared anhydrous hydrogen fluoride, and, following Lavoisier's school, considered fluoric acid to be a compound of water with the oxide of a new element—"fluorium." In 1810 A. Ampère wrote to H. Davy suggesting "many ingenious and original arguments" in favour of the analogy between hydrochloric and hydrofluoric acids. Ampère concluded that hydrofluoric acid contained no oxygen. Ampère's ideas were established by H. Davy's experimental work, 1813, and the unknown element was named "fluorine" by analogy with chlorine. Many unsuccessful attempts have been made to isolate this element by the electrolysis of hydrofluoric acid (H. Davy); electrolysis of fused potassium fluoride (E. Fremy, 1856); the action of chlorine on silver fluoride (H. Davy), and on mercuric fluoride in fluorspar vessels (G. J. and T. Knox, 1836); heating iodine with silver fluoride (H. Kämmerer, 1862); heating silver fluoride (H. Davy); the electrolysis of liquid fused silver fluoride (G. Gore, 1869); heating the unstable uranium fluoride, UF_5, in oxygen (H. B. Dixon); the action of oxygen on fused calcium fluoride (E. Fremy, 1856); heating lead fluoride, PbF_4, and also cerium fluoride, CeF_4 (B. Brauner, 1881); etc. The feat was accomplished in 1886, when H. Moissan isolated the gas by the electrolysis of a solution of potassium fluoride in liquid hydrogen fluoride, and thus solved, what H. E. Roscoe called, "one of the most difficult problems in modern chemistry."

Preparation.—When an electric current is passed through a concentrated solution of hydrogen chloride, chlorine is liberated at the anode, and hydrogen at the cathode. When aqueous hydrofluoric acid is treated in the same way, water alone is decomposed, for oxygen is liberated at the anode, and hydrogen at the cathode. The anhydrous acid does not conduct electricity, and it cannot therefore be electrolyzed. Moissan found that if potassium fluoride be dissolved in the liquid hydrogen fluoride, the solution conducts electricity, and when electrolyzed, hydrogen is evolved at the cathode, and fluorine at the anode. The primary products of the electrolysis are fluorine at the anode, potassium at the cathode: $2KHF_2 = 2HF + 2K + F_2$. The potassium reacts with the hydrogen fluoride reforming potassium fluoride and liberating hydrogen: $2K + 2HF = 2KF + H_2$.

The electrolysis was first conducted in a U-tube made from an alloy of platinum and iridium which is less attacked by fluorine than platinum alone. Later experiments showed that a tube of copper could be employed. The copper is attacked by the fluorine, forming a surface crust of copper fluoride which protects the tube from further action. Electrodes of the platinum iridium alloy are used. A tube is illustrated in Fig. 119. The open ends of the tube are closed with fluorspar stoppers ground to fit the tubes and bored with holes which grip the electrodes. The joints are made air-tight with lead washers and shellac. The U-tube, during the electrolysis, is surrounded

with a glass cylinder *B*, into which liquid methyl chloride is passed from a steel cylinder *via* the tube *A*, Fig 120 Liquid methyl chloride boils at —23°, and it escapes through an exit tube The fluorine is passed through a spiral platinum tube also placed in a bath of evaporating liquid methyl chloride, *C* This cools the spiral tube down to about —50°, and condenses gaseous hydrogen fluoride, which escapes with the fluorine from the U tube The fluorine then travels through two platinum tubes, *D* and *E*, containing lumps of sodium fluoride, which remove the least traces of hydrogen fluoride A glass cylinder is placed outside each of the two cylinders containing methyl chloride The outer cylinders contain a few lumps of calcium chloride, so as to dry the air in the vicinity of the cold jacket, and prevent the deposition of frost on the cylinders.

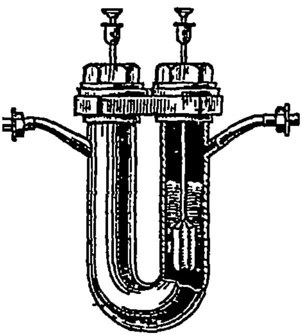


FIG 119 —Tube for the Electrolysis of Hydrofluoric Acid

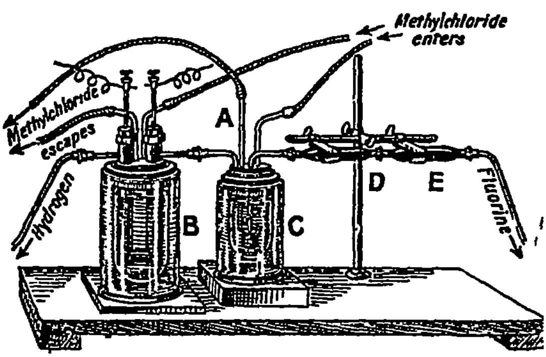


FIG 120 —Moissan's Process for Fluorine

Properties —Fluorine is a light canary yellow gas which condenses to a clear yellow liquid boiling at —187°, and freezes to a pale yellow solid melting at —233°, at —252° the solid is colourless Fluorine is probably the most active element known It combines with hydrogen with explosion, even in the dark, and at low temperatures It decomposes water, forming hydrogen fluoride, and liberates oxygen highly charged with ozone Sulphur melts and takes fire in the gas. Iodine, bromine, phosphorus, arsenic, and antimony combine with the gas with incandescence, so do crystalline silicon, amorphous boron, powdered charcoal All metals are acted upon by the gas, some take fire spontaneously, others when heated to, say, 300°, *e.g* gold and platinum Fluorine also liberates chlorine from sodium chloride and from carbon tetrachloride, CCl_4 Liquid fluorine has no action on silicon, phosphorus, sulphur, and glass Fluorine is one of the few elements which is not known to form an oxide

No compound of fluorine with chlorine is known Bromine forms bromine trifluoride, BrF_3, and iodine forms iodine pentafluoride, IF_5 Chlorine can unite with iodine, but there is no reliable evidence of the existence of compounds of bromine with chlorine The known compounds of iodine with chlorine are iodine monochloride, ICl, and iodine trichloride, ICl_3, and with bromine iodine monobromide, IBr Higher iodine bromides have been reported, but their existence has not been clearly established A similar remark applies to the so called bromine monochloride

Atomic and molecular weight of fluorine—The combining weight of fluorine has been established by converting calcium fluoride, potassium fluoride, sodium fluoride, etc, into the corresponding sulphates J B A. Dumas (1860) found that 1 gram of pure potassium fluoride furnishes 1 4991 gram of potassium sulphate Given the atomic weights of potassium 39 1, sulphur 32 07, oxygen 16, it follows that if x denotes the combining weight of fluorine with 39 1 grams of potassium, 1 : 1 4991 $= 2KF : K_2SO_4 = 2(39\ 1 + x) : 174\ 27$, or, $x = 19$ The best determinations range between 18 97 and 19 14, and the best representative value of the combining weight of fluorine is taken to be 19 No known volatile compound of fluorine contains less than 19 parts of fluorine per molecule, and accordingly this same number is taken to represent the atomic weight The vapour density of fluorine is 1 31 (air = 1), that is, $28\ 755 \times 1\ 31 = 37\ 7$ ($H_2 = 2$) The molecule of fluorine is therefore represented by F_2

Questions

1 Potassium iodide is liable to contain potassium iodate, and calomel is liable to contain corrosive sublimate How do you account for the presence of these impurities, and how would you test for their presence ?—*St Andrews Univ*

2 Name two minerals containing fluorine and write their formulæ How and by whom was fluorine first isolated ? How is hydrofluoric acid prepared, in what form is it usually used in the laboratory, and how is it employed in etching ? —*Princeton Univ , U S A*

3 By what method is hydrogen fluoride prepared in a state of purity ? Contrast its properties with those of the hydrides of chlorine, bromine, and iodine How has fluorine been isolated ?—*London Univ*

4 How would you prepare a specimen of pure hydrogen iodide ? Give examples of its reducing action —*St Andrews Univ*

5 What is meant by the term " catalytic agent " ? Describe the use of such an agent in the preparation of hydrogen bromide What is the chief source of iodine at the present time ?—*Cornell Univ , U S A*

6 What do you understand by a reversible chemical action ? Cite examples Point out the conditions affecting the course of the action —*St Andrews Univ*

7 Explain the nature, from a chemical point of view, of the chief operations involved in the production of a photograph —*London Univ*

8 Describe the preparation and properties of hydrogen bromide and hydrogen iodide Why are these gases not commonly prepared by reactions similar to that used in the ordinary preparation of hydrogen chloride ?—*Victoria Univ , Manchester*

9 Describe the effects observed when chlorine water is added (*a*) to mercurous chloride, (*b*) to potassium iodide solution What inference do you draw about the reactions that have taken place ? Why ?—*Sheffield Scientific School, U S A*

10 Define and give examples of thermal dissociation, kinetic equilibrium, reversible reaction, electrolysis and reduction —*Princeton Univ , U S A*

11 What experiments have been made with the object of isolating fluorine ? and how do you account for their failure ?—*London Univ*

12 Describe and explain the appearances observed when (*a*) sodium chloride, (*b*) sodium bromide, (*c*) sodium iodide is heated with concentrated sulphuric acid What operations would be necessary to cause hydrogen to combine with chlorine bromine, and iodine respectively ?—*London Univ*

13 The rate of chemical change may be altered by (*a*) temperature, (*b*) catalysis, (*c*) solution Describe accurately one experiment illustrating the change in rate of a reaction, which may be brought about by each of these factors —*London Univ*

14 Describe a convenient laboratory method for preparing chlorine How would you dry and collect the gas ? What action has chlorine on (*a*) antimony, (*b*) an aqueous solution of potassium bromide, (*c*) an aqueous solution of potassium hydroxide ?—*Victoria Univ , Manchester*

15 Sketch the apparatus you would employ and explain, with all essential practical details, the method you would adopt to prepare a saturated solution of hydriodic acid —*Board of Educ*

CHAPTER XV

The Oxides and Oxyacids of Chlorine, Bromine, and Iodine

§ 1 Chlorine Monoxide

Molecular weight, Cl_2O = 86 92 Boiling point, + 5° Relative vapour density (H_2 = 2), 86 5, (air = 1) 3·01

Preparation—This compound is prepared by passing a slow current of dry chlorine from the apparatus *AB*, Fig 121, through a glass tube *C* containing dry precipitated mercuric oxide previously heated for about an hour to about 400° The tube is cooled by immersion in cold water, and the issuing gas is passed through a U tube *D* cooled with ice and salt Brownish yellow mercuric oxychloride and chlorine monoxide are formed $2HgO + 2Cl_2 = Hg_2OCl_2 + Cl_2O$ The gas condenses in the U-tube If freshly precipitated mercuric oxide be used, the chlorine acts too vigorously, forming mercuric chloride and liberating oxygen—may be explosively, if the mercuric oxide be in coarse fragments, the reaction is too slow

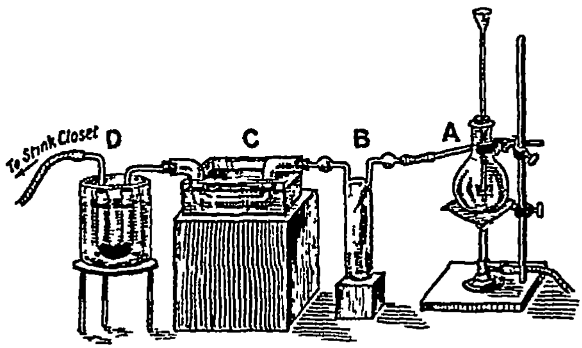


Fig 121 —Preparation of Chlorine monoxide

Properties—Chlorine monoxide is a pale orange yellow gas with the greenish tinge characteristic of chlorine Its smell is not unlike (but is easily distinguishable from) that of chlorine One volume of water dissolves 200 volumes of the gas at 0° and the solution behaves like an acid —hypochlorous acid, HClO $Cl_2O + H_2O = 2HOCl$ Hypochlorous acid forms salts—hypochlorites—with the bases. The hypochlorite radicle "ClO" then acts as a monad Hence chlorine monoxide is also hypochlorous anhydride If the gas be passed through a tube surrounded with a mixture of ice and salt the gas condenses to a reddish brown liquid between 19° and 20° The liquid boils at 5° and 738 mm pressure Both the liquid and the gas are very unstable Mere contact of the gas with sulphur, phosphorus, and many carbon compounds—*e g* caoutchouc, turpentine, etc —lead to decomposition with explosive violence With

granular calcium chloride it forms calcium hypochlorite and chlorine $CaCl_2 + 2Cl_2O = Ca(OCl)_2 + 2Cl_2$ The liquid is more liable to explosion than the gas, for it may explode with a slight mechanical shock, *e g* when poured from one vessel to another As indicated above, the liquid can be distilled under reduced pressure, and it may be exposed to sunlight without decomposition in perfectly clean vessels

Composition —Pass a stream of the gas through a capillary tube with three bulbs, *and gently heat the tube in front of the first bulb* The gas decomposes before it enters the bulbs, the capillary tube prevents an explosion When the bulbs are filled with the products of decomposition, each bulb can be sealed off and the contents examined The free chlorine in each bulb is absorbed by potassium hydroxide, the results show that two volumes of chlorine accompany every one volume of oxygen Since according to Avogadro's hypothesis, equal volumes of these gases contain the same number of molecules, and since both chlorine and oxygen have two atom molecules, it follows that the molecule of chlorine monoxide has two atoms of chlorine per one atom of oxygen The vapour density of chlorine monoxide is 86 92 ($H_2=2$) This corresponds with a molecule containing two atoms of chlorine and one atom of oxygen, hence the formula is written Cl_2O The action of heat is to resolve two volumes of the gas into two volumes of chlorine and one volume of oxygen $2Cl_2O \rightarrow 2Cl_2 + O_2$.

§ 2 Hypochlorous Acid.

The action of chlorine on cold water —It is probable that a *cold* aqueous solution of chlorine decomposes, forming a mixture of hydrochloric and hypochlorous acids For equilibrium $Cl_2 + H_2O \rightleftharpoons HCl + HOCl$ This is evidenced by the fact that chlorine water reacts acid with litmus before it bleaches, and some hypochlorous acid can be separated by distillation However, the amount of the two acids present when the system is in equilibrium is very small If one of the products, say hydrochloric acid, be removed, the equilibrium is disturbed and the reaction proceeds in the direction needed to re-establish equilibrium If freshly precipitated mercuric oxide, for example, be present, the hydrochloric acid reacts with the mercuric oxide, forming mercuric chloride, $HgCl_2$ The hypochlorous acid is such a weak acid that it has practically no action on the mercuric oxide The action of chlorine on water containing mercuric oxide is therefore represented $HgO + H_2O + 2Cl_2 \rightleftharpoons HgCl_2 + 2HOCl$ Similarly, if calcium carbonate be suspended in the water $CaCO_3 + H_2O + 2Cl_2 \rightleftharpoons CaCl_2 + CO_2 + 2HOCl$. If the resulting liquid be distilled, a dilute solution of hypochlorous acid passes over

The action of chlorine on cold solutions of alkali hydroxides —A similar action occurs if cold water containing a little potassium hydroxide be treated with chlorine, but both acids are neutralized

$$H_2O + Cl_2 \rightleftharpoons \begin{cases} HOCl \\ HCl \end{cases} \quad \text{and} \quad \begin{matrix} HOCl + KOH = KOCl + H_2O \\ HCl + KOH = KCl + H_2O \end{matrix}$$

equilibrium is disturbed, and the reaction from left to right is almost complete The net result of the reaction is represented $Cl_2 + 2KOH \rightleftharpoons KCl + KOCl + H_2O$ The resulting solution is called *eau de Javelles*

so named because it was prepared by C L Berthollet's process at Javel, a suburb of Paris, in 1792 In 1834, A J Balard proved that eau de Javelles is a mixture of potassium chloride and hypochlorite The solution is sometimes used for bleaching purposes If sodium hydroxide be employed, as suggested by A G Labarraque, in 1820, the so called "chlorinated soda," or *Labarraque's solution*, is obtained The electrolysis of cold solutions of sodium or potassium chloride furnishes sodium or potassium hydroxide and chlorine If the products of electrolysis are allowed to intermix, sodium or potassium hypochlorites are formed in a similar manner

Preparation —As indicated above, a little hypochlorous acid accompanied by hydrochloric acid is formed when chlorine is dissolved in water Hypochlorous acid can be obtained by distilling a solution of bleaching powder or eau de Javelles with dilute nitric acid Almost all the hypochlorous acid is liberated by the dilute nitric acid $KOCl + HNO_3 \rightleftharpoons KNO_3 + HOCl$, while the chloride is scarcely affected since so little nitric acid is present $KCl + HNO_3 \rightleftharpoons KNO_3 + HCl$ To avoid this latter reaction, a weak acid like boric acid is more efficient than nitric acid because a very great excess of boric acid must be present before appreciable quantities of hydrochloric acid can be set free

Properties.—Pure hypochlorous acid free from water has not been obtained because the acid is so very unstable The aqueous solution can be concentrated to a golden-yellow liquid, but only the yellowish solutions containing about 5 per cent of HOCl can be distilled without decomposition. More concentrated solutions are decomposed on warming into chloric ($HClO_3$) and hydrochloric acids $3HOCl = HClO_3 + 2HCl$, followed by the reaction $HCl + HOCl = H_2O + Cl_2$, for hypochlorous acid is decomposed by acids, and with hydrochloric acid the chlorine of both acids is set free Hypochlorous acid is a monobasic acid and forms salts with bases The radicle "ClO" is a monad, and its compounds with the bases are called **hypochlorites** Highly concentrated solutions of sodium hydroxide, saturated with chlorine and evaporated at a low temperature, furnish needle like crystals of sodium **hypochlorite**—$NaOCl.6H_2O$—contaminated with about 3 per cent. of sodium chloride Similarly, by the action of chlorine on milk of lime, and further concentrating the resulting solution by the alternate addition of more lime and chlorine, crystals of **calcium hypochlorite**—$Ca(OCl)_2$—have been obtained The crystals are not deliquescent, and keep well Hypochlorous acid is so feeble in strength that the carbon dioxide of the air is sufficient to displace the acid from hypochlorites

The oxidizing action of hypochlorous acid —When warmed, hypochlorous acid not only furnishes chloric acid—$HClO_3$—as indicated above, but it is also decomposed with the evolution of oxygen $2HOCl = 2HCl + O_2$ This reaction is particularly active in sunlight, and in the presence of oxidizing agents Thus with silver oxide $Ag_2O + 2HOCl = 2AgCl + H_2O + O_2$ If a little nickel or cobalt nitrate solution be added to water containing hypochlorous acid and the mixture warmed in a flask, oxygen is evolved $2HOCl = 2HCl + O_2$ The cobalt salt acts as a catalytic agent The mechanism of the reaction is generally supposed to involve the concurrent reactions corresponding with the transformations of the cobalt oxide $CoO \rightarrow Co_2O_3 \rightarrow CoO \rightarrow Co_2O_3 \rightarrow$ etc When oxygen

is prepared by this process, bleaching powder suspended in water is the usual source of the hypochlorous acid In illustration of the oxidizing action of hypochlorous acid, calcium hypochlorite or bleaching powder may be boiled for some time with a solution of lead acetate, puce coloured lead dioxide, PbO_2, will be precipitated, and if boiled with a solution of a manganous salt, manganese dioxide, MnO_2, will be precipitated More prolonged boiling may give a green solution of calcium manganate, or a pink coloured solution of calcium permanganate $Ca(MnO_4)_2$

The rapid decomposition of hypochlorous acid in sunlight renders it probable that the action of light on chlorine water results in the formation of the hypochlorous acid by hydrolysis $Cl_2 + H_2O = HCl + HOCl$, is at once decomposed $2HOCl = 2HCl + O_2$, so that the hydrolysis goes to completion, and leaves, as final products, hydrochloric acid, water and oxygen

Test —When an excess of mercury is shaken up with an aqueous solution of hypochlorous acid, a brownish-yellow precipitate of mercuric oxychloride, $HgO\,HgCl_2$, is formed, this is decomposed by dilute hydrochloric acid—mercurous chloride passes into solution With chlorine water, mercury gives a white precipitate of mercurous chloride, HgCl, hence the reaction can be used to distinguish and even to estimate hypochlorous acid in the presence of free chlorine in solution

§ 3 Bleaching Powder.

History —The bleaching properties of Javel water were discovered by C L Berthollet in 1785 The facts were communicated to James Watt in Paris about the same time, and Watt soon afterwards brought the news to Glasgow In 1798, Charles Tennant patented a process for the use of cheaper lime in place of potash The patent was later declared void because lime had been used for the same purpose in Lancashire prior to Tennant's patent

The action of chlorine on calcium hydroxide —If chlorine be allowed to act upon an aqueous solution of a bivalent base, say calcium hydroxide, in place of potassium or sodium hydroxide, a molecule of each of the two monobasic acids, formed by the action of chlorine on water, *is neutralized* by one molecule of the base, and what seems to be a mixed salt is formed:

$$Ca<^{OH}_{OH} + {HOCl \atop HCl} = Ca<^{OCl}_{Cl} + 2H_2O$$

The salt Cl—Ca—OCl is called "bleaching powder" or "chloride of lime" This substance may also be regarded as a molecular compound of calcium chloride with calcium hypochlorite $CaCl_2$, $Ca(OCl)_2$ The constitution of bleaching powder has been much discussed, and the subject is yet far from being definitely settled It is very probable that bleaching powder contains but little calcium chloride because (1) the chlorine can be expelled from it by the action of carbon dioxide This would not be the case if calcium chloride were *present*, (2) calcium chloride is very deliquescent, bleaching powder is not, and calcium chloride is readily dissolved by alcohol, whereas an alcoholic *solution* of bleaching powder contains but traces of calcium chloride *Under very favourable circumstances* lime can be saturated with no more than 43½ per cent of available chlorine The facts correspond with the formula Ca(OCl)Cl first suggested,

without proof, by W Odling in 1861 Since the available chlorine in commercial bleaching powder usually ranges between 36 and 38 per cent, it is evident that the calcium hydroxide, $Ca(OH)_2$, is not completely saturated with chlorine, and that some free calcium hydroxide is present Hence commercial bleaching powder is best represented as $Ca(OCl)Cl + nCa(OH)_2$, where n is very nearly one half, or $2Ca(OCl)Cl + Ca(OH)_2$

Preparation —Bleaching powder is made on a large scale by the action of chlorine on slaked lime, $Ca(OH)_2$ The lime is spread in 3 or 4 inch layers on perforated shelves in a large chamber, and then raked into furrows *Chlorine is led through the chambers At first the absorption* of chlorine is rapid, but it afterwards slows down The lime is then turned over from time to time so as to expose a fresh surface After standing for 12 to 24 hours a shower of fine dust lime is blown into the chamber to absorb the excess of chlorine The amount of chlorine absorbed is never so complete as is represented by the equation $Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O$ The commercial value of the bleaching powder depends on the amount of available chlorine it contains The amount of available chlorine depends upon the method of preparation, temperature, etc If the temperature be kept between 30° and 40°, a bleaching powder containing about 40 per cent of available chlorine has been prepared.

Evaluation of bleaching powder —The process for the determination of the available chloride depends upon the fact that sodium arsenite is oxidized to sodium arsenate by an aqueous solution of bleaching powder Hence a standard solution of sodium arsenite is added to a known amount of an aqueous solution bleaching powder until the solution no longer gives a blue coloration with iodized starch paper This shows that no available chlorine is present The amount of sodium arsenite used in the experiment is related with the bleaching powder by the following equation $Ca(OCl)Cl + Na_3AsO_3 = Na_3AsO_4 + CaCl_2$, and the theoretical amount of $Ca(OCl)Cl$ can therefore be readily computed

The action of water and acids —If bleaching powder be treated with cold water, it forms a strongly alkaline solution, and insoluble calcium hydroxide remains It is probable that the action is due to the hydrolysis of the calcium hypochlorite $2Ca(OCl)Cl = Ca(OCl)_2 + CaCl_2$, followed by $Ca(OCl)_2 + 2H_2O = Ca(OH)_2 + 2HOCl$ If the bleaching powder be treated with a very dilute acid, hypochlorous acid, $HOCl$, is formed $Ca(OCl)Cl + HCl = CaCl_2 + HOCl$ If an excess of acid be present, the hypochlorous acid is decomposed, forming water and chlorine $HOCl + HCl = H_2O + Cl_2$

Bleaching powder decomposes when exposed to atmospheric moisture The carbon dioxide of the air also reacts like a feeble acid as indicated above Bleaching powder also decomposes slowly when kept in a well stoppered bottle When heated with ammonia, nitrogen is obtained $2NH_3 + 3Ca(OCl)Cl = 3H_2O + 3CaCl_2 + N_2$, and when boiled with water and a little cobalt salt, oxygen is obtained as indicated above Thus, hypochlorous acid, chlorine, and oxygen can be obtained from bleaching powder

Bleaching —In bleaching by eau de Javelles or by bleaching powder, the fabric is steeped in a dilute aqueous solution of the bleaching agent, and then in dilute acid. Hypochlorous acid is thus produced, and then free chlorine The free chlorine does its work within the fibres of the wet fabric as

indicated on p 239 The bleaching action of hypochlorous acid is generally stated to be twice as great as that of the chlorine it contains, supposing the latter were free $2Cl_2 + 2H_2O = 4HCl + O_2$, $4HOCl = 4HCl + 2O_2$ But it must be remembered that two atoms of chlorine are needed to form one molecule of HOCl, since an equivalent amount of HCl is formed at the same time

§ 4 Potassium and Barium Chlorates

The manufacture of potassium chlorate, $KClO_3$.—We have seen that when chlorine is passed into a cold solution of potassium hydroxide, a mixture of potassium chloride and hypochlorite is formed, and when the solution of the hypochlorite is boiled, it decomposes, forming a mixture of potassium chlorate and chloride A similar result is obtained when chlorine is passed into a *hot* (70°) aqueous solution of potassium hydroxide $6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O$, and the two salts—potassium chloride and potassium chlorate—can be separated by fractional crystallization Potassium chlorate is far less soluble than the corresponding chloride, p 17 C L. Berthollet (1786-8) first isolated this salt, although it appears to have been known to J R Glauber (1658) who mistook it for saltpetre The above method of preparation is due to J L Gay-Lussac (1818)

Liebig's process of manufacture —It will be observed that the amount of chlorate obtained from a given amount of potassium hydroxide is small because one molecule of potassium chlorate is accompanied by five molecules of potassium chloride as by-product This loss is serious because the potassium hydroxide is relatively expensive This led J von Liebig (1842) to modify the process It is cheaper to substitute a hot solution of slaked lime in water for the potassium hydroxide solution In that case $6Ca(OH)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O$ The clear solution of calcium chlorate and chloride is concentrated a little by evaporation, and a slight excess of potassium chloride is added Potassium chlorate has but one tenth the solubility of the corresponding calcium salt, and is far less soluble than the other two chlorides, hence, by a further concentration of the solution, the least soluble potassium chlorate separates $Ca(ClO_3)_2 + 2KCl = 2KClO_3 + CaCl_2$ The potassium chlorate so obtained is purified by recrystallization

The electrolytic process of manufacture —The old process of J von Liebig is now almost displaced by the electrolytic process. Hot solutions of potassium chloride are electrolyzed The initial and end stages of the reactions are represented $KCl + 3H_2O = KClO_3 + 3H_2$, but no doubt chlorine is first formed (p 236), then potassium hypochlorite, and finally potassium chlorate The sparingly soluble potassium chlorate crystallizes from the solution during the electrolysis, and thus gives trouble Since 100 c c of water at 20° dissolve about 99 grams of sodium chlorate; and 100 c c of water, about 7 2 grams of potassium chlorate, it is best to first prepare sodium chlorate by the electrolysis of sodium chloride, and then treat the solution with potassium chloride as in the case of calcium chlorate described above Potassium chlorate can be readily isolated by fractional crystallization

The solubility and the action of heat on potassium chlorate have been described previously Potassium chlorate is used medicinally, in the

manufacture of matches, fireworks, and explosives, as an oxidizing agent in chemical processes, for the preparation of small quantities of oxygen, etc

Barium chlorate, $Ba(ClO_3)_2$ —This salt can be prepared by the electrolysis of a solution of barium chloride, or by the action of chlorine on a hot solution of barium hydroxide, or on water containing barium carbonate in suspension The separation of barium chlorate and barium chloride by fractional crystallization is rather difficult because the two salts are almost equally soluble in water It is best to cool the crystallizing solution to 0°, at which temperature 100 parts of a saturated solution contain 16 9 grams of barium chlorate, and 100 grams of a saturated solution contain 24 grams of barium chloride, at 10°, the corresponding solubilities are 21 and 25, and at 20°, 25 and 26

§ 5 Chloric Acid

Preparation —The chlorates, as we have seen, were first made by C L. Berthollet, and J L Gay Lussac (1814) obtained chloric acid by the following process A solution of, say, 80 grams of barium chlorate in 170 c c of water is treated with an equivalent quantity of sulphuric acid (24 3 grams of H_2SO_4 in 200 c c of water), when barium sulphate and chloric acid are formed $Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3$ The clear solution of chloric acid is decanted from the precipitated barium sulphate, and concentrated by evaporation in vacuo over sulphuric acid Solutions containing more than about 40 per cent $HClO_3$ cannot be prepared, because the chloric acid then decomposes spontaneously into free chlorine, oxygen, perchloric acid—$HClO_4$—and water The first action is probably $2HClO_3 = HClO_4 + HClO_2$, the chlorous acid, $HClO_2$, so formed reacts with the chloric acid, forming chlorine peroxide, ClO_2 $HClO_2 + HClO_3 \rightleftharpoons H_2O + 2ClO_2$, and the chlorine peroxide breaks down into chlorine and oxygen $2ClO_2 = Cl_2 + 2O_2$, as indicated below The initial and end products of the completed reaction are represented $3HClO_3 = HClO_4 + H_2O + Cl_2 + 2O_2$

Properties —The concentrated solution of chloric acid so prepared is a colourless viscid liquid with a pungent smell It readily decomposes on exposure to light The solution is stable in darkness provided organic matter be absent Wood, paper, etc, decompose the acid at once—very often with spontaneous combustion Blue litmus is first reddened and then bleached by the acid Even in a dilute solution, chloric acid is a powerful bleaching agent The acid is monobasic, forming a series of salts—chlorates—where ClO_3 acts as a univalent radicle The anhydride of the acid—chlorine pentoxide, Cl_2O_5—is not known

The chlorates —The chlorates are powerful oxidizing agents An explosion may occur if a chlorate be mixed with organic matter, charcoal, sulphur, etc, and the mixture struck with a hammer, or heated Hence mixtures of chlorates with such materials must not be ground together with a pestle and mortar The materials should be ground separately, and then carefully mixed on paper with a feather Phosphorus in contact with a chlorate may explode spontaneously Thus if a drop of a solution of phosphorus in carbon disulphide be allowed to fall on a little potassium chlorate, a loud explosion occurs as soon as the carbon disulphide has evaporated

The chlorates are all soluble in water Potassium chlorate is one of the least soluble of the chlorates The salts are fairly stable, but decompose into chlorides and oxygen when heated The chlorates are recognized by giving no precipitate with silver nitrate, although, after ignition, the silver nitrate will give a precipitate of silver chloride with an aqueous solution of the residue If a few drops of a solution of indigo sulphate be added to an aqueous solution of a chlorate, and the liquid be acidified with sulphuric acid, and sulphurous acid, or a sulphite be added, the chloric acid is reduced to a lower chlorine oxide which bleaches the blue colour of the indigo

Composition —The composition of chloric acid was established by J S Stas' analyses of silver chlorate A known amount of silver chlorate was reduced to the chloride by the action of sulphurous acid Previous analyses had established the exact composition of silver chloride Stas found that 100 grams of silver chlorate furnished

Silver chloride—AgCl	74 9205 grams
Oxygen	25 0795 ,,
Silver chlorate	100 0000 ,,

The molecular weight of silver chloride is 143 43, and the atomic weight of oxygen is 16 By division, 74 9206 — 143 34 = 0 52, and 25 0795 — 16 = 1 58 Hence the ratio of silver chloride to oxygen in the silver chlorate is as 1 3, or the empirical formula of silver chloride is $AgClO_3$, and of the acid $HClO_3$ The molecular weight of the acid has not been determined satisfactorily

§ 6 Chlorine Peroxide.

Molecular weight, ClO_2 = 67 46 Melting point, −79°, boiling point, 0° Vapour density, 67 29 (H_2 = 2), 2 39 (air = 1)

Preparation —While studying the action of concentrated sulphuric acid upon potassium chlorate, H Davy (1811) found that a highly explosive gas was produced Finely powdered potassium chlorate is gradually added to concentrated sulphuric acid in a small flask or retort *A*, Fig 122 The salt dissolves, producing a reddish-brown liquid, but no gas is evolved if the liquid be kept cold When the solution is gradually warmed, by placing the retort in a vessel, *B*, of warm water, taking care not to heat the glass above the level of the liquid in the retort, chlorine peroxide is evolved as a gas The first action of the sulphuric acid is to form chloric acid

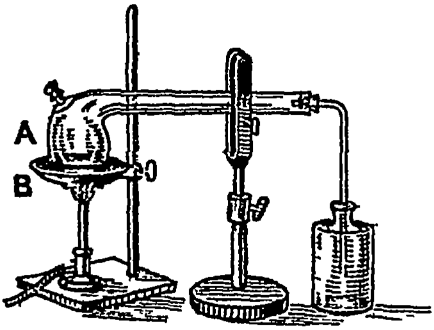


FIG 122 —Preparation of Chlorine Peroxide

$KClO_3 + H_2SO_4 = KHSO_4 + HClO_3$, and the chloric acid is then decomposed into perchloric acid, $HClO_4$, chlorine peroxide, and water $3HClO_3 = HClO_4 + 2ClO_2 + H_2O$

Properties —Chlorine peroxide is a reddish-yellow gas with an unpleasant smell which produces headache The gas is much heavier than

air, and it is collected by the upward displacement of air, *C*, since it decomposes in contact with mercury, and it is fairly soluble in water. Water at 4° dissolves about twenty times its volume of the gas. When the solution is cooled to lower temperatures a crystalline hydrate separates—possibly as $ClO_2 \cdot 8H_2O$. On standing, in the dark, an aqueous solution of chlorine peroxide forms a mixture of chloric and hydrochloric acids. When the gas is cooled, it condenses to a dark red liquid which boils at 9°, and the liquid can be frozen to orange coloured crystals melting at −79°. Chlorine peroxide is very unstable. It decomposes with explosive violence if an electric spark be passed through the gas, or if a hot wire be introduced into the gas. Chlorine peroxide also decomposes into its elements if it be exposed to the light. The gas is liable to suddenly explode, especially if in the liquid or solid condition, or if organic matter be present. Chlorine peroxide is a powerful oxidizing agent—a piece of phosphorus, sugar, or other combustible takes fire spontaneously in the gas.

Two well-known experiments may be cited to illustrate this. Place some crystals of potassium chlorate at the bottom of a test glass, and half fill the vessel with water. A few lumps of yellow phosphorus are dropped into the glass, and concentrated sulphuric acid is allowed to flow through a tube funnel on to the chlorate. The bubbles of chlorine peroxide which are evolved produce bright flashes of light when they come in contact with the phosphorus under the water. Again, powdered sugar and potassium chlorate are mixed with a feather on a sheet of paper and placed on a stone slab. When a drop of sulphuric acid is allowed to fall upon the mass, the chlorine peroxide which is formed ignites the sugar, and the flame rapidly spreads throughout the mass.

Composition.—Gay Lussac determined the composition of chlorine peroxide by passing the gas through a capillary tube with three bulbs of known capacity. The capillary tube was heated before the gas entered the bulbs. Decomposition took place in the capillary tube without explosion. The bulbs therefore contained the decomposition products of the chlorine peroxide—chlorine and oxygen. The chlorine was determined by absorption with potassium hydroxide and the oxygen in a gas measuring tube. It was found that 100 volumes of the peroxide furnished 100.6 volumes of oxygen and 49.3 volumes of chlorine. Hence it was inferred that

$$\underbrace{2ClO_2}_{2\text{ Vols.}} = \underbrace{Cl_2}_{1\text{ Vol.}} + \underbrace{2O_2}_{2\text{ Vols.}}$$

and by the application of Avogadro's hypothesis, that equal volumes contain an equal number of molecules, and that oxygen and chlorine molecules each contain two atoms, it follows that the formula of chlorine peroxide is ClO_2. This is confirmed by the vapour density—67.29—which corresponds with the molecule ClO_2, not Cl_2O_4. The molecular weights of the gas in water, and in carbon tetrachloride, as solvents, agree with the formula ClO_2. Thus the chlorine in chlorine peroxide appears, at first sight, to be quadrivalent.

Chlorites and chlorous acid.—When an aqueous solution of chlorine peroxide is treated with an alkali, say potassium hydroxide, a mixture of potassium chlorite and chlorate is formed: $2KOH + 2ClO_2 = KClO_2 + KClO_3 + H_2O$, and if potassium peroxide be employed, potassium chlorite and oxygen are produced: $K_2O_4 + 2ClO_2 = 2KClO_2 + 2O_2$. The acidified solution probably contains chlorous acid, $HClO_2$. The chlorites are readily decomposed. Lead chlorite $Pb(ClO_2)_2$ at 100° decomposes

with detonation The soluble chlorites bleach vegetable colouring matters, even after the addition of arsenious acid This is not the case with the hypochlorites Pure chlorous acid has not been prepared, and the corresponding anhydride—chlorine trioxide, Cl_2O_3—is unknown

H Davy prepared a gas by the action of concentrated hydrochloric acid upon potassium chlorate, which he believed to be chlorine trioxide, with the composition Cl_2O_3, and which was termed euchlorine Euchlorine, however, is a mixture of chlorine with chlorine peroxide in varying proportions [1] A mixture of potassium chlorate and hydrochloric acid is often employed in the laboratory as an oxidizing agent

§ 7 Perchloric Acid.

Preparation —Perchloric acid is formed when chloric acid is heated or exposed to light $3HClO_3 = Cl_2 + HClO_4 + 2O_2 + H_2O$ and by the action of sulphuric acid on, say, potassium perchlorate $2KClO_4 + H_2SO_4 \rightleftharpoons K_2SO_4 + 2HClO_4$ Count Stadion first made perchloric acid in 1816 Potassium perchlorate is prepared, as indicated on p 171, by the action of heat on potassium chlorate

If 50 grams of pure dry potassium perchlorate be distilled under reduced pressure in a 300 c c distilling flask with 150 to 175 grams of concentrated (96 to 97½ per cent) sulphuric acid, a white crystalline mass of $HClO_4.H_2O$ collects in the receiver The water is formed by the decomposition of the acid during the distillation. By the redistillation of this product under reduced pressure, pure perchloric acid can be obtained

Electrolytic process of manufacture.—Perchloric acid and the perchlorates can be prepared by the electrolysis of the chloric acid and the chlorates respectively The chlorate is not directly oxidized, as was once supposed The chlorate ions appear at the anode during the electrolysis $KClO_3 = K^{\cdot} + ClO_3'$, when the ions are discharged at the electrodes, the potassium reacts with the water forming hydrogen and the chlorate ion forms chloric acid which decomposes as indicated above into perchloric and chlorous acids and oxygen $2ClO_3 + H_2O = HClO_4 + HClO_2 + O_2$ The oxygen so formed oxidizes the chlorous acid back to chloric acid $HClO_2 + O = HClO_3$ The initial and end products are therefore represented $2KClO_3 + 2H_2O = 2KClO_4 + 2H_2$

Properties —Perchloric acid is a volatile colourless fuming liquid, specific gravity 1 764 at 22°, boils at 14° to 18° under a pressure of 15 to 20 mm., and freezes at −112° to a crystalline solid If a drop of the acid be brought in contact with paper or wood, instantaneous and violent inflammation occurs, if a drop of the acid be brought in contact with charcoal, a violent explosion occurs Perchloric acid produces serious wounds in contact with the skin If the acid be distilled at ordinary pressures, the liquid may gradually become darker and darker in colour, and finally explode violently The pure acid is also said to be liable to explode after standing some days

[1] D I Mendeléeff thinks that some chlorine trioxide, Cl_2O_3—vapour density 119 —is present because the vapour density of euchlorine, according to L Pebal, is about 80, and the vapour density of chlorine peroxide is 67 3, and of chlorine, 71 Mixtures of these two would give too low a vapour density Some of the chlorine peroxide, however, may be present as Cl_2O_4

The action of water.—When dropped into water, the two combine with a hissing sound, and the evolution of much heat. $HClO_4 + Aq = HClO_4aq + 20.3$ Cals. Perchloric acid forms five hydrates containing respectively 1, 2, 2.5, 3, and 3.5 molecules of water. The monohydrate is formed by adding water to the pure acid until crystals begin to appear. This hydrate melts at 50°, and freezes at the same temperature, forming long needle-like crystals. Solutions more concentrated than 71.6 per cent. $HClO_4$ lose $HClO_4$ when distilled, and less concentrated solutions lose water. The "constant boiling acid" contains 71.6 per cent. of $HClO_4$, boils at 203°, and distils unchanged in composition. It fumes slightly in air, and may be preserved indefinitely, even in light. Perchloric acid slowly volatilizes at 138° without decomposition.

Thermochemistry of the oxychlorine acids.—Perchloric acid is not so powerful an oxidizing agent as chloric acid, and this in turn is less vigorous than hypochlorous acid. This corresponds with the greater amount of available energy per atom of available oxygen associated with hypochlorous acid than with either chloric or perchloric acid. For instance, the thermochemical equations are represented:

$$HOClaq = HClaq + O + 9.3 \text{ Cals.}, \text{ or } 9.3 \text{ Cals. per atom of oxygen}$$
$$HClO_3aq = HClaq + 3O + 15.3 \text{ Cals.}, \text{ or } 5.1 \text{ Cals. per atom of oxygen}$$
$$HClO_4aq = HClaq + 4O + 0.7 \text{ Cals.}, \text{ or } 0.2 \text{ Cals. per atom of oxygen}$$

Since the bleaching effect of these reagents is supposed to depend upon the action of nascent oxygen, it follows that in this case there is no particular need for the assumption that atomic oxygen is more active than molecular oxygen, because the "nascent oxygen" is associated with a larger amount of available energy, which can do chemical work. The available energy of each acid must be *added to* that which free oxygen could give if it alone were performing the same oxidation; according to the principle of maximum work, the amount of energy degraded during a chemical reaction measures the "tendency of a reaction to take place." Hence the greater oxidizing properties of these acids must, at least in part, be due to the greater amount of available energy associated with their "nascent oxygen" during decomposition.

Perchlorates.—An aqueous solution of perchloric acid reddens litmus, and forms salts—perchlorates—where the radicle "ClO_4" is univalent. Hence perchloric acid is monobasic. The potassium salt is one of the least soluble perchlorates. It is practically insoluble in absolute alcohol. When perchloric acid is added to an alcoholic solution of a soluble potassium salt, potassium perchlorate is quantitatively precipitated. The weight of potassium perchlorate so obtained enables the amount of potassium in the given solution to be computed. Unlike the chlorates, the perchlorates are not decomposed by hydrochloric acid; nor do they yield an explosive gas when warmed with concentrated sulphuric acid. They are not reduced to chlorides by sulphur dioxide; and they require a higher temperature for their decomposition than the corresponding chlorates. Sodium perchlorate as well as sodium chlorate occur with sodium nitrate in native Chili saltpetre.

Composition.—10.03 grams of perchloric acid were dissolved in water, and treated with a small excess of potassium carbonate. The solution was evaporated to dryness with a slight excess of acetic acid, and washed with

absolute alcohol to remove the potassium acetate The residual potassium perchlorate was dried and weighed The potassium perchlorate was ignited to drive off the oxygen The results were

Potassium perchlorate	13 8326 grams
Potassium chloride, KCl	7 4434 ,,
Oxygen	6 3892 ,,

The composition of the residual potassium chloride, by a previous analysis, is known to be KCl with a molecular weight 74 56 Divide the amount of oxygen by 16, and the amount of potassium chloride by 74 56 to get the atomic ratio KCl O This was found to be KCl O = 1 4 corresponding with the empirical formula $KClO_4$ for the potassium salt, and $HClO_4$ for the acid If the acid is monobasic the formula must be $HClO_4$, if dibasic, $H_2Cl_2O_8$, etc If the acid is dibasic, it would *probably* be possible to prepare an acid salt, $KHCl_2O_8$ The acid salt has not been made, hence the analytical data may be taken as circumstantial evidence that the molecular formula of the salt is $KClO_4$ Thus, it is possible to estimate the probable molecular formula of an acid by chemical analysis, and mutatis mutandis also of a base By the same argument it has been shown that the formula of hydrofluoric acid is probably H_2F_2, because it behaves as a dibasic acid

Chlorine heptoxide—Perchloric anhydride—Cl_2O_7—is obtained by digesting perchloric acid with phosphorus pentoxide cooled to —10° for some time, and then distilling the mixture at 82° The chlorine heptoxide condenses to a colourless volatile oil which decomposes in a few days It is explosive, and reacts with water, forming perchloric acid Chlorine heptoxide was isolated by Michael and Conn in 1900

§ 8 The Valency of Chlorine

The oxides and oxyacids of chlorine so far considered are

Oxides		Acids	
Chlorine monoxide	Cl_2O	Hypochlorous acid	$HClO$
[Chlorine trioxide	Cl_2O_3]	Chlorous acid	$HClO_2$
Chlorine peroxide	ClO_2		
[Chlorine pentoxide	Cl_2O_5]	Chloric acid	$HClO_3$
Chlorine heptoxide	Cl_2O_7	Perchloric acid	$HClO_4$

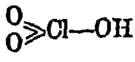
The anhydrides indicated in the brackets have not been prepared, while hypochlorous and chloric acids are only known in solution The constitution of these compounds is by no means clear Some base the graphic formulæ on bivalent oxygen and univalent chlorine

$$\underset{\text{Chloric acid}}{HO—O—O—Cl} \qquad \underset{\text{Perchloric acid}}{HO—O—O—O—Cl}$$

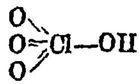
Carbon compounds with chains of oxygen atoms are usually less stable the longer the chain of oxygen Here the contrary is the case, HOCl is least stable, and HOOOOCl is the most stable of these acids Some, therefore, suppose that the chain formulæ are improbable, and that chlorine monoxide is constituted like nitrogen monoxide, chlorine peroxide like nitrogen peroxide, and chloric acid like nitric acid, namely—

$$\underset{\text{Chlorine monoxide}}{{}^{Cl}_{Cl}{>}O} \qquad \underset{\text{Chloric acid}}{HO—Cl{<}^{O}_{O}} \qquad \underset{\text{Perchloric acid.}}{HO—Cl{<}^{O}_{O}{>}O}$$

where chlorine may be uni- and ter valent. The nitrogen oxides will be described later. Others consider that in chloric acid the chlorine is quinquevalent, and in perchloric acid, septavalent.



Chloric acid



Perchloric acid

The existence of compounds like iodine trichloride, etc., are difficult to explain other than by assuming that the iodine is multi valent.

§ 9 Hypobromous and Hypoiodous Acids

When iodine or bromine is added to a cold aqueous solution of ammonia, or to cold solutions of potassium, sodium, calcium, or barium hydroxides, a colourless liquid is obtained which possesses bleaching qualities. This solution resembles, in many respects, corresponding solutions obtained with chlorine. Hence it is inferred that in the case of, say, iodine, hypoiodite and iodide are formed, and in the case of bromine, hypobromite and bromide are formed. Thus with iodine $2KOH + I_2 \rightleftharpoons KI + KOI + H_2O$. A dilute solution of the corresponding acids can be made by shaking mercuric oxide with a cold aqueous solution of bromine or iodine with water. With bromine $HgO + H_2O + 2Br_2 = HgBr_2 + 2HOBr$. The aqueous solutions of these acids are very unstable, particularly in the case of the hypoiodites and hypoiodous acid. An aqueous solution of hypoiodous acid decomposes into hydriodic and iodic acids, and these react together forming free iodine. The aqueous solution of potassium hypoiodite decomposes at ordinary temperatures in a few hours into potassium iodide and iodate. $3KOI = 2KI + KIO_3$. Hypobromous acid decomposes at 60° into bromine and water, but the aqueous solution can be distilled at 40° in vacuo. Substances resembling bleaching powder have been formed by the action of bromine and of iodine upon slaked lime. "Iodine bleaching powder" is probably best represented, $Ca(IO)I$, and "bromine bleaching powder," $Ca(OBr)Br$.

Bromous acid.—What appears to be a solution of bromous acid, $HBrO_2$, is formed when bromine water is agitated with a concentrated solution of silver nitrate. It is probable that hypobromous acid is first formed $AgNO_3 + Br_2 + H_2O = HOBr + AgBr + HNO_3$, and that the hypobromous acid is subsequently oxidized $2AgNO_3 + Br_2 + H_2O + HOBr = HBrO_2 + 2HNO_3 + 2AgBr$. However, neither the acid nor its salts have been isolated.

§ 10 Bromic Acid

Potassium bromate—$KBrO_3$.—This salt can be made by dropping 80 grams of bromine slowly into a cold solution of 62 grams of potassium hydroxide and 62 grams of water. The cold yellow solution soon deposits crystals of bromate. $6KOH + 3Br_2 = 5KBr + KBrO_3 + 3H_2O$. The crystals are filtered off, and purified by recrystallization from 130 c.c. of boiling water. The mother liquid contains potassium bromide, KBr. If an aqueous solution of barium hydroxide be substituted for potassium hydroxide, barium bromate is obtained $Ba(BrO_3)_2.H_2O$.

Bromic acid, $HBrO_3$—An aqueous solution of bromic acid is made by treating barium bromate with the calculated quantity of sulphuric acid $Ba(BrO_3)_2 + H_2SO_4 = BaSO_4 + 2HBrO_3$ The solution is decanted from the precipitated barium sulphate and the aqueous solution concentrated by evaporation in vacuo until it contains about 50 per cent of the acid If the concentration be carried further, or the acid be heated, it decomposes into bromine, oxygen, and water

The bromates resemble the chlorates, but when heated, there is no sign of the formation of perbromates analogous with perchlorates The decomposition proceeds $2KBrO_3 = 2KBr + 3O_2$ Some of the metallic bromates, when heated, give the metallic oxide, bromine, and oxygen $2Mg(BrO_3)_2 = 2MgO + 2Br_2 + 5O_2$ Bromine water in aqueous solution is oxidized to bromic acid by the action of chlorine $Br_2 + 6H_2O + 5Cl_2 = 10HCl + 2HBrO_3$ The bromic acid so obtained is mixed with hydrochloric acid

§ 11 Iodic Acid

Potassium iodate, KIO_3—Potassium iodate can be made by the direct action of iodine on potassium chlorate $2KClO_3 + I_2 = 2KIO_3 + Cl_2$ This reaction illustrates how iodine is able to replace chlorine in its oxygen compounds, although the reverse action occurs with the hydrogen compounds. $2HI + Cl_2 = 2HCl + I_2$ These differences correspond with the difference in the heats of formation (or decomposition) of the hydracids and the oxyacids

Hydracids	Oxyacids
$H + Cl = HCl + 22.0$ Cals	$H + Cl + 3O + Aq = HClO_3aq + 24.0$ Cals
$H + Br = HBr + 8.4$ Cals	$H + Br + 3O + Aq = HBrO_3aq + 12.4$ Cals
$H + I = HI - 6.0$ Cals	$H + I + 3O + Aq = HIO_3aq + 42.6$ Cals

Hence the order of the stability of the hydracids is HCl, HBr, HI, and of the oxyacids $HIO_3, HClO_3, HBrO_3$

To prepare potassium iodate, dissolve, say, 25 grams of potassium chlorate in a 200 c c flask with 120 c c of boiling water, add 26 grams of iodine, and 1 c c of concentrated nitric acid to the hot solution In a few minutes, chemical action begins and a stream of chlorine escapes from the flask When the violence of the reaction has subsided, boil the solution to drive off the chlorine Let the solution cool Potassium iodate is less soluble in cold water than potassium chlorate, and accordingly most of the potassium iodate can be separated by crystallization Filter off the crystals of potassium iodate, dissolve the crystals in hot water, neutralize the solution with potassium hydroxide, and cool the solution Fairly pure potassium iodate crystallizes from the solution

Barium iodate, $Ba(IO_3)_2$—This salt can be prepared by dissolving iodine in an aqueous solution of barium hydroxide, or by the addition of barium chlorate to an aqueous solution of potassium iodate White granular barium iodate is precipitated.

The preparation of iodic acid, HIO_3—Iodic acid can be made by the process described for bromic acid, of course substituting iodine for bromine, for instance, by the action of dilute sulphuric acid on barium iodate, or by the action of chlorine on water containing iodine in suspension, or by the action of an aqueous solution of chloric acid on iodine Iodic acid, however, is usually made by the direct oxidation of iodine with

nitric acid. The end products are usually represented $10HNO_3 + I_2 = 2HIO_3 + 10NO_2 + 4H_2O$ There is, however, no doubt that the reaction is much more complex, and the equation does little more than show how iodic acid can be one product of the action of nitric acid on iodine

Add 32 grams of powdered iodine, in small quantities at a time, to 130 grams of concentrated colourless nitric acid heated in a 500 c c flask fitted with a long neck to act as a condenser A current of air, carbon dioxide, or oxygen is passed through the mixture to remove the nitrogen oxides as fast as they are formed When the iodine has all dissolved, and a white precipitate of iodic acid has taken its place, let the solution cool Collect the solid iodic acid on an asbestos filter Dissolve the acid in the least possible quantity of hot water again filter and allow the solution to recrystallize from a 20 per cent solution of nitric acid If the iodic acid so prepared be not colourless, it must be again crystallized

The properties of iodic acid—Iodic acid is a white crystalline solid readily soluble in water The aqueous solution first reddens blue litmus, and then bleaches the colour If iodic acid be treated with concentrated sulphuric acid until iodine begins to be evolved, a yellow solid is obtained which, after washing with water, and then with ether, furnishes numbers corresponding with iodine dioxide, IO_2, or iodine tetroxide, I_2O_4—the molecular weight has not been determined Iodic acid does not give a blue colour with starch In some cases, it behaves as a monobasic acid forming salts—iodates Most of the iodates are insoluble in water, and behave like the bromates when heated. The iodates form a series of "acid salts" with iodic acid, thus

KIO_3	$KIO_3.HIO_3$	$KIO_3.2HIO_3$
Normal iodate	Uniacid iodate	Biacid iodate

These facts have led to the belief that, unlike the corresponding chloric acid, iodic acid is polybasic—may be $H_2I_2O_6$ Iodine may be ter- or quinque valent in iodic acid, that is,

$$HO—I\Big<{}^{O—O}_{O—O}\Big>I—OH \quad \text{or} \quad HO—I\ll{}^{O}_{O}$$

But really the constitution of the acid is not known with any degree of probability When iodic acid is heated to about 170°, it decomposes with the loss of water forming iodine pentoxide, I_2O_5, thus $2HIO_3 = H_2O + I_2O_5$ This substance is a white crystalline solid which forms iodic acid when it is dissolved in water, hence, iodine pentoxide is iodic anhydride It is more stable than the other oxides of bromine or chlorine, but it decomposes into its elements above 200°

Iodic acid is an oxidizing agent It reduces hydrogen sulphide with the liberation of iodine $2HIO_3 + 5H_2S = 5S + 6H_2O + I_2$, and with hydriodic acid $HIO_3 + 5HI = 3I_2 + 3H_2O$, and with sulphur dioxide $2HIO_3 + 5SO_2 + 4H_2O = 5H_2SO_4 + I_2$. This latter reaction is used as a test for iodates The solution is first acidified with hydrochloric acid to liberate the iodic acid, and then mixed with starch paste Sulphurous acid, or an alkaline sulphite, is then added drop by drop The liberated iodine forms "blue starch iodide," the characteristic reaction of iodine

The period of induction—The last-named reaction is very interesting because the iodine does not appear immediately the substances are mixed, there is a well defined period of time—period of induction—between the

moment the reacting substances are mixed, and the moment iodine makes its appearance The duration of the interval is dependent upon the concentrations of the solutions. This can be demonstrated in the following manner Dissolve 1 8 gram of iodic acid in a litre of water, also prepare a litre of an aqueous solution of 0 9 gram of sodium sulphite, $Na_2SO_3.7H_2O$, 10 per cent sulphuric acid, and 9 5 grams of starch made into a paste with hot water Add 100 c c of each solution to separate beakers, and mix the two Note the time when the solutions are mixed. Count the seconds which pass before the starch blue appears. Dilute each solution to 0 8, 0 6, 0 4, 0 2 of its former concentration, and repeat the experiments with the diluted solutions Plot the results as has been done in Fig 123 If the concentration and temperature be constant, the same results can always be reproduced It is supposed that the first action is due to the reduction of the iodic acid to hydriodic acid $3H_2SO_3 + HIO_3 = 3H_2SO_4 + HI$, and when all the sulphurous acid has been oxidized, this reaction is followed by the reduction of the hydriodic acid by the excess of iodic acid $HIO_3 + 5HI = 3H_2O + 3I_2$ The first reaction—oxidation of sulphurous acid—must be nearly completed before the second one can start, because, as indicated above, the iodine with sulphurous acid reforms hydriodic acid Since the maximum amount of iodic and sulphurous acids are present at the start, the first-named reaction must be fastest at the beginning, and afterwards gradually slow down Again, since the velocity of a reaction is proportional to the amount of the reacting substances present in the system, the second reaction will be the slowest at the start, and gradually become faster The speed of formation of the iodine is therefore the resultant velocity of two consecutive reactions, and the belated appearance of the iodine—the period of induction—corresponds with the time required for the first reaction to make enough hydriodic acid to enable the second reaction to make sufficient iodine to colour the starch To summarize the successive steps in the reduction of iodic acid to iodine $2HIO_3 \rightarrow 2HI \rightarrow I_2$, where HI represents an "intermediate compound" characteristic of consecutive reactions generally

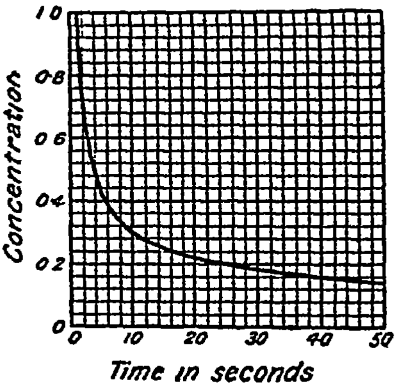
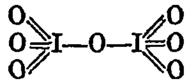


FIG 123—Period of Induction

§ 12 Periodic Acid, and Perbromic Acid

It was once thought that perbromic acid—$HBrO_4$—could be made by the action of bromine on perchloric acid, but the evidence is not satisfactory, and it is therefore somewhat doubtful if perbromic acid has yet been prepared. Periodic acid—HIO_4—has not been made, but a large number of related salts, classed as periodates, are known These are somewhat difficult to understand because of their complexity Our study of perchloric acid may help us a little. Starting from the assumption that iodine

is septivalent in periodic anhydride—I_2O_7, the constitutional formula of iodine heptoxide will be



This compound has not yet been prepared, when it is, we infer that it will be analogous with the known corresponding compound of chlorine—Cl_2O_7 By adding water step by step to this oxide, we can imagine the series of acids with the corresponding salts represented in the following table Many salts have been isolated even when the corresponding acids are unknown

TABLE XIII —THE PERIODIC ACIDS

I_2O_7 with	Compounds formed	Empirical formula of acid	Name of acid	Salts
$1H_2O$	$I_2O_6(OH)_2$, or $2IO_3OH$	HIO_4	Meta periodic acid	KIO_4, $AgIO_4$, etc
$2H_2O$	$I_2O_5(OH)_4$	$H_4I_2O_9$	Dimeso periodic acid	No salts known
$3H_2O$	$I_2O_4(OH)_6$, or $2IO_2(OH)_3$	H_3IO_5	Meso periodic acid	Ag_3IO_5, $Pb_3(IO_5)_2$; etc
$4H_2O$	$I_2O_3(OH)_8$	$H_8I_2O_{11}$	Dipara periodic acid	Salts have been reported, probably mixtures
$5H_2O$	$I_2O_2(OH)_{10}$, or $2IO(OH)_5$	H_5IO_6	Para periodic acid	Ag_5IO_6, $Ag_2H_3IO_6$, etc
$6H_2O$	$I_2O(OH)_{12}$	$H_{12}I_2O_{13}$	Diortho periodic acid	Salts have been reported, probably mixtures
$7H_2O$	$I_2(OH)_{14}$, or $2I(OH)_7$	H_7IO_7	Ortho periodic acid	No salts known

Nomenclature of the periodic acids and the periodates —When *one* anhydride forms a series of acids by union with different amounts of water, the acid containing most water is called the ortho-acid—from the Greek ὀρθός (orthos) regular the other acids have prefixes, making para-acid—from the Greek παρά (para), beside, meso-acid—from the Greek μέρος (meros), middle, intermediate; and meta-acid—from the Greek μετά (meta) beyond, less than the highest. The *di-acids are supposed to be formed by abstraction of one molecule of water from* two molecules of acid It will be evident that if the acids are polybasic, we can imagine the available hydrogen atoms replaced one by one If all the available hydrogen atoms are replaced by bases, the normal salt is obtained, if only *one* of the available hydrogen atoms is replaced, the primary salt, if two, the secondary salt, if three, the tertiary salt

Secondary sodium para-periodate has the composition $Na_2H_3IO_6$ thus corresponding with para-periodic acid, or $HIO_4 \cdot 4H_2O$ It can be prepared as a sparingly soluble salt by passing chlorine into an aqueous solution of sodium iodate and sodium hydroxide $NaIO_3 + 3NaOH + Cl_2 = 2NaCl + Na_2H_3IO_6$ The periodate is dissolved in nitric acid and silver nitrate is added to the solution Crystals of silver metaperiodate—$AgIO_4$—corresponding with meta-periodic acid, separate when the solution is concentrated by evaporation

Para-periodic acid —When silver meta periodate is boiled with water, an insoluble salt, secondary silver para-periodate, is formed along with

paraperiodic acid, H_5IO_6, or $HIO_4\,2H_2O$ Thus $2AgIO_4+4H_2O=Ag_2H_3IO_6 + H_5IO_6$ When the clear solution is concentrated, deliquescent crystals of the para-periodic acid are obtained This acid melts at 133°, and decomposes into iodine pentoxide, water, and oxygen at 150° The water cannot be expelled by heat because oxygen is evolved along with the water

A small quantity of potassium periodate is said to occur in native Chili saltpetre, along with some sodium iodate

§ 13 The Halogen Family of Elements.

Fluorine, chlorine, bromine, and iodine together form a remarkable family of elements The whole group is sometimes called the **halogens**—from the Greek ἅλς (hals), sea salt, γεννάω (gennao), I produce This name was applied because these elements—principally chlorine, bromine, and iodine—are found in sea-water, and the sodium salts resemble sea salt (sodium chloride) The fluorides, chlorides, bromides, and iodides are often called the halides The family relationship of the halogens is illustrated by—

(1) The *similarity* in the chemical and physical properties of the elements and their corresponding compounds

(2) The *gradual transition* of chemical and physical properties such that if the elements be arranged in order F, Cl, Br, I, the variation in any particular property in passing from fluorine to iodine nearly always proceeds in the same order, and that is the order of their atomic weights

The relationship in the physical properties of the halogens can best be emphasized by the tabular scheme

TABLE XIV —THE PHYSICAL PROPERTIES OF THE HALOGENS

Property	Fluorine	Chlorine	Bromine	Iodine
Atomic weight	19	35 46	79 92	126 92
State of aggregation	Gas	Gas	Liquid	Solid
Melting point	−233°	−102°	−7 3°	+114°
Boiling point	−187°	−33 6°	58° to 63°	183°
Specific gravity	1 14 (liq)	1 55 (liq)	3 19 (liq)	5 (solid)
Atomic volume [1]	16 7	22 9	25 1	25 6
Colour of gas	Pale yellow	Greenish yellow	Brownish red	Violet
Solubility (100 c c water at 20°) dissolves grams	Decomposes water	0 0001	0 032	0 00015

All the halogens form compounds with hydrogen, and the readiness with which union occurs decreases as the atomic weight increases The properties of the halogen acids and their salts show as striking a relationship as the elements themselves, and are shown in Table XV, next page

The boiling point and composition of the acid of constant composition of hydrofluoric acid is exceptional Hydrogen fluoride, HF, appears to be polymerized below 88° Again, while the affinity of the halogens for hydrogen decreases with increasing atomic weight, the reverse is the case

[1] Atomic volume is the atomic weight divided by the specific gravity

with oxygen But with oxygen the relationship is not so clearly defined Thus although fluorine forms no known compound with oxygen, numerous compounds of oxygen with chlorine have been obtained, and, judging by the known compounds with oxygen, the affinity of bromine for oxygen appears to be less, not greater, than is the case with chlorine, although we must remember that bromine has not been investigated so much as chlorine Chlorine, bromine, and iodine form an unstable series of compounds analogous with hypochlorites and chlorates, but the bromine analogue of perchlorates has not been prepared

TABLE XV —THE PROPERTIES OF THE HALOID ACIDS

Property	Hydrogen fluoride	Hydrogen chloride	Hydrogen bromide	Hydrogen iodide
Molecular weight	20	36 46	80 93	127 93
Boiling point	19 4°	−83 4°	−67 1°	−35 5(4 atm)
Melting point	−92 5°	−111 4°	−88 1 °	−50 9°
Solubility in water	35 3 %	42 %	−49 %	57 %
Specific gravity saturated aq sol	1 15	1 21	1 49	1 70
Boiling point aq sol	111° (43 %)	110° (20 %)	126° (47 %)	127° (57%)
Dissociates at	—	1500°	800°	180°
Heat of formation (Cals)	+38 5 gas	+22 0 gas	+12 3 gas	+0 4 gas
Heat of formation of K salt (Cals)	110 6	105 7	95 3	80 1
Potassium salt melts	885°	790°	750°	705°
Calcium salt melts	1330°	780°	760	740°
Solubility Ag salt (20°) per 100 c c. water	181 8	0 016	0·00084	0 000028
Solubility Ca salt per 100 c c solution	0 16	42 7	58 8	67 6

Questions

1 You are required to establish experimentally the validity or otherwise of the following equation $6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O$ Describe in detail the methods you would employ —*Science and Art Dept*

2 Describe the preparation and properties of the oxides and oxy acids of chlorine What is understood by an *endothermic compound*, and by what pecu liarities are such compounds distinguished ?—*Aberdeen Univ*

3 Make out a *table* comparing the various members of the chlorine family —*Princeton Univ*, *U S A*

4 Calculate the percentage of "active chlorine" in a sample of bleaching powder from the following data 10 grams of the powder was extracted with 500 c cm of water, 25 c cm of the extract when added to an acidified solution of potassium iodide set free iodine equivalent to 32 7 c cm of $\frac{1}{10}$ N solution of sodium thiosulphate (Cl = 35 5, I = 127) —*Univ North Wales*

5 Describe the methods by which iodic and periodic acids are best prepared, and discuss the evidence afforded by these compounds as to the valency of iodine —*Science and Art Dept*

6 How can chlorine be prepared from bleaching powder? What is the effect of passing chlorine into an aqueous solution of (*a*) hydrogen sulphide (*b*) sulphur dioxide, (*c*) potassium hydroxide, (*d*) potassium iodide ?—*Sheffield Univ*

7 Point out the chemical similarity between chlorine, bromine and iodine What is this group called ? How is each of these elements set free from a salt containing it ?—*Sheffield Scientific School, U S A*

8 Three salts are known which contain oxygen in addition to potassium and chlorine Write the formulæ of these salts and explain how each salt can be (a) prepared, (b) recognized, (c) made to furnish chlorine —*Sheffield Univ*

9 Make a chart of the halogens (a) in the order of the atomic weights, (b) giving the colour of each, (c) giving the physical state of each, (d) and the relative stability of the common acids —*Amherst Coll, U S A*

10 Give the law of multiple proportion, illustrating from the series of chlorine oxyacids —*Amherst Coll, U S A*

11 It has long been known that the decomposition of potassium chlorate is effected at a lower temperature in the presence of certain metallic oxides, that bleaching powder will yield oxygen in the presence of cobalt oxide, and that oxygen is evolved from hydrogen peroxide by the addition of finely divided silver or platinum What explanations can you give of such changes ?—*Science and Art Dept*

12 Compare and contrast the properties of hydrogen fluoride and of hydrogen chloride, and the properties of the perchlorates with those of the periodates —*Owens Coll*

13 "The most important compounds of chlorine with hydrogen and oxygen are hypochlorous acid, chloric acid, and perchloric acid" Describe how you would prepare each of these acids from chlorine as the starting product By what reactions could you distinguish hydrochloric acid from hypochlorous acid ?—*London Univ*

14 How do you account for the greater stability of perchloric as compared with chloric acid ?—*Board of Educ*

15 What is meant by saying that fluorine is a "halogen" ? Compare its properties with those of the other halogens, and describe the preparation of two fluorides, one of a metal, and the other of a non metal, beginning with the fluorine in the form of fluorspar —*London Univ*

16 Trace the successive reactions involved in the production of hypochlorites, chlorates, and perchlorates, discussing for each stage the chemical change which occurs in it, and the conditions under which it takes place By what properties are these salts severally distinguished ?—*Board of Educ*

NOTE FOR PAGE 240

A Smith and A W C Menzies (1910) showed that the vapour pressure of a mixture of calomel and mercury will be equal to the sum of the vapour pressure of mercury and calomel if there be no dissociation, and less than this sum if dissociation of the calomel vapour occurs Experiment showed that the observed vapour pressure of the mixture is less than that calculated for complete dissociation This was traced to a slight lowering of the vapour pressure of mercury owing to its dissolving a little calomel Allowing for this, Smith and Menzies' measurements give numbers in close agreement with the view that the vapour of calomel is completely dissociated

CHAPTER XVI

ELECTROLYSIS AND THE IONIC HYPOTHESIS

§ 1 The Products of Electrolysis.

ONE or both of the products of electrolysis may be an insoluble solid, a soluble liquid, a gas, etc When an insoluble solid is formed it will either stick to the electrode, or fall to the bottom of the electrolytic cell (Fig 5), if a gas, not too soluble in the electrolyte, be formed, the gas can be collected as indicated in Fig 17 Soluble substances are not usually visible The soluble matters can often be isolated more or less completely by surrounding the proper electrode with a porous pot which retards the diffusion and mixing of the products separated at the two electrodes This is done, for example, in the industrial preparation of chlorine

It will be remembered that during the electrolysis of copper sulphate, the products of the electrolysis were copper, sulphuric acid, and oxygen This is more than was present in the copper sulphate used at the start It is therefore assumed, as a trial hypothesis, that ions Cu and SO_4 are produced at the electrodes during the passage of the current, that the copper cation carries a positive charge of electricity, and the SO_4 anion a negative charge Consequently, the Cu ion will be found at the negative electrode, and the SO_4 ion at the positive electrode The ions are de electrified at the electrodes the Cu at the cathode, and the SO_4 at the anode The de electrified copper ions are deposited as metallic copper about the cathode, and the de electrified SO_4, at the anode, reacts at once with the solvent (water), producing sulphuric acid and oxygen $2SO_4 + 2H_2O = 2H_2SO_4 + O_2$. When an aqueous solution of potassium nitrate is electrolyzed, potassium hydroxide and gaseous hydrogen are formed at the cathode, and nitric acid and oxygen at the anode It is assumed that the potassium nitrate is first decomposed into two electrified ions, K and NO_3, at the electrodes, and that the K ion, when de electrified, reacts with water at the cathode, producing potassium hydroxide and hydrogen, and the NO_3 ion, when de electrified at the anode, reacts with water, giving nitric acid and oxygen $4NO_3 + 2H_2O = 4HNO_3 + O_2$

Again, if a solution of silver nitrate be electrolyzed with silver electrodes, metallic silver is deposited at the cathode, and the nitric acid produced at the anode attacks and dissolves the cathode forming silver nitrate This explains how the total concentration of a solution of silver nitrate does not alter if electrolyzed in a cell with a silver anode The nitric acid produces more silver nitrate as fast as it is formed Similar remarks apply to the electrolysis of copper sulphate with a copper anode, etc

Electroplating—If copper sulphate were used as electrolyte in place of zinc sulphate, Fig 5, metallic copper would be precipitated at the cathode, and sulphuric acid would have been formed about the anode, with silver nitrate, metallic silver would collect about the cathode, and nitric acid about the anode If a plate of silver be used as the anode during the electrolysis of silver nitrate, metallic silver will be dissolved by the nitric acid as fast as the acid is formed Thus, the concentration of the silver nitrate in the solution will remain unchanged and metallic silver will be transported to the cathode This is the principle of the method of electroplating In the case of "silver-plating" a firmer and more uniform deposit of silver is obtained by using a solution of silver cyanide in potassium cyanide as the electrolyte in place of silver nitrate The article to be plated, say a brass spoon is attached to a wire and dipped in the solution of silver salt, and this is made the cathode A bar or sheet of silver is made the anode A rather weak electric current is sent through the electrolyte The electrolyte is decomposed and silver (cation) is deposited on the article to be plated (cathode), the anion collecting at the anode dissolves the silver anode, and thus keeps the strength of the electrolyte unchanged What is dissolved at the anode is deposited at the cathode Salts of other metals—nickel, gold, copper, platinum, etc—can be used as electrolytes in a similar manner, and accordingly articles can be nickel-plated, gold-plated, etc The plated articles may be afterwards burnished

We first inquire if there is any relation between the quantity of electricity passing through an electrolytic cell and the amount of decomposition In order to fix a standard of measurement, let the quantity of electricity required to deposit 0 001118 gram of silver be called a **coulomb** Hence 108 grams of silver, that is, a chemical equivalent of silver, will be deposited by 96,540 coulombs of electricity This amount of electricity is often called a **farad** **The quantity of an element liberated by the passage of one farad of electricity is called the electro-chemical equivalent of the element**

The so called "hydraulic analogy" of an electric current might here be cited to remind the student what he probably learned in "Physics" The quantity of water flowing through a pipe can be expressed in gallons or cubic feet per second, in a similar way, quantity of electricity may be expressed in terms of coulombs per second An electric current carrying one coulomb per second is called an ampere A coulomb by the same analogy would correspond with, say, a gallon or cubic foot of water The total quantity of water delivered by a pipe is determined by the "head" or pressure of water, so that in order to pass a certain number of gallons per second through a given pipe, a certain pressure must be applied to overcome the frictional resistance of the pipe In the same way, a certain electromotive force—electrical pressure—is required on account of the resistance offered by the wire to the flow of electricity Just as water pressure is measured in pounds per square inch, or in feet "difference of level" or "head," so the unit of electrical pressure, the volt, is the difference of potential needed to produce a current of one ampere in a conductor whose resistance is equivalent to that of a uniform column of 14 45 grams of mercury, 106 3 cm long The resistance of such a column is called an ohm Hence a volt is the electric pressure required to produce a current of one ampere in a conductor of one ohm resistance The terms voltage, electrical pressure, and electromotive force are generally applied synonymously to an electric current, or, if the current is not directly under consideration the term difference of potential is used It is of course needless to dwell on the fact that the analogy used above in comparing an electric current with a moving fluid is merely a convenience It is probable that electricity is not a fluid, and the analogy must not be carried much further

§ 2 Faraday's Laws of Definite Electrolytic Action.

M Faraday (1834) found that the amount of chemical work done by an electric current is directly proportional to the quantity of electricity which passes through the electrolyte If one farad leads to separation of 108 grams of silver, two farads will lead to the separation of 216 grams of silver, and so on. Similar results are obtained with other electrolytes Hence said Faraday " the chemical decomposing action of a current is constant for a given quantity of electricity " Or " the quantity of chemical decomposition is exactly proportionate to the quantity of electricity which has passed through the electrolyte ," and consequently, " the products of decomposition afford a very excellent and valuable measure of the electricity concerned in their evolution " The increase in the weight of, say, the negative electrode during the electrolysis of silver nitrate, or copper sulphate owing to the deposition of metallic silver or copper respectively, is a measure of the quantity of electricity which has passed through the system A cell specially designed for such measurements is called a silver voltameter or a copper voltameter respectively

Provided there are no disturbing secondary actions, the amount of electro decomposition is not affected by the strength (or intensity) of the current, the time the current is passing, the concentration of the solution, the nature of the dissolved substance, nor by the temperature. The same quantity of electricity will always liberate the same quantity of the elements stated. The accuracy of the law is said to have been established for " currents so small that a century would be required for the separation of a milligram of hydrogen " and in large electrochemical works, the law is continually being verified by the passage of millions of coulombs. In every case, the law describes the phenomena exactly

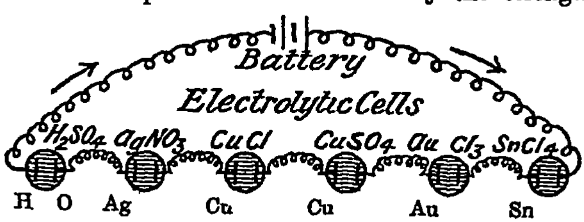


Fig 124 —Experiment illustrating Faraday's Laws

Again, let a current be *simultaneously* passed through six cells containing respectively dilute sulphuric acid, aqueous solutions of silver nitrate, cuprous chloride, cupric sulphate, gold chloride, and stannic chloride The experiment is conducted by arranging the electrolytic cells as illustrated in the plan, Fig 124. After about half an hour's electrolysis the amounts of the different elements collected at the cathode can be weighed or measured. The results will be very nearly

	Dilute H_2SO_4		$AgNO_3$	$CuCl$ (acid sol)	$CuSO_4$	$AuCl_3$	$SnCl_4$	
	Cathode	Anode						
	Hydrogen	Oxygen	Silver	Copper	Copper	Gold	Tin	
Amount found	0.0266	0.2126	2.9370	1.6900	0.8440	1.7476	0·7554	gram
If H = 1	1	8	108	63.5	31.8	65.7	29.8	"
Atomic weight	1.01	16	107.9	63.6	63.6	197.2	119	
Valency	1	2	1	1	2	3	4	

Accordingly, chemically equivalent quantities of the different elements (that is, atomic weight — valency) are liberated by the passage of

the same quantity of electricity Consequently, the electrochemical equivalent of an element is numerically the same as the chemical equivalent

At first sight, this result appears to contradict the principle of excluded perpetual motion, because, if the current from a $Zn|H_2SO_4|Pt$ battery be sent through an indefinite number of electrolytic cells containing dilute sulphuric acid, the same amount of hydrogen would be liberated in each, and sufficient hydrogen could be collected to furnish, on combustion, enough heat to evaporate the solution of zinc sulphate in the battery to dryness, to transform the zinc sulphate to metallic zinc and sulphuric acid, and so reconstruct the battery, and have some hydrogen remaining in excess The experiment would fail The current would not traverse an indefinitely large number of cells W H Wollaston showed in 1801 that electrical energy is the product of two factors, and that "quantity of electricity" is only one of these factors Faraday's law describes the influence of "quantity of electricity" upon electrolysis It says nothing about the electrical pressure—the electromotive force, described in volts—required to drive the necessary *quantity* of electricity through the system Hence Faraday's work may be summarized **The same quantity of electricity, passing through one or more electrolytes connected up in series, will liberate in each cell chemically equivalent amounts of the products of electrolysis, provided the electromotive force permit the necessary current to be maintained** It might here be added that, for reasons which will be discussed later, a certain specific electrical pressure or voltage —called the decomposition voltage—is required to electrolyze a given solution, thus, hydrochloric acid requires about $1\frac{1}{4}$ volts, and sodium chloride about 4 volts

Let each positive charge of electricity be represented by a small dot, and each negative charge by a small dash at the upper right hand corner of the chemical symbol for an element, then, a silver ion will be written Ag , *a zinc ion by Zn* , a nitrate ion, NO_3', and a sulphate ion by SO_4'' In the electrolysis of aqueous solutions of salts, etc, the separation of an ion at one electrode is always attended by the separation of a chemically equivalent ion or ions at the other electrode For instance, with zinc chloride, for every *Zn* which is de electrified at the cathode, two Cl' ions will be de electrified at the anode

We have just seen that the electrochemical and chemical equivalents are numerically the same, and therefore the electrochemical *equivalent* of an element is obtained by dividing the atomic weight by the valency The same quantity of electricity—positive or negative—must therefore be carried by each univalent atom, and accompany it in all its movements in the electrolytic fluid This quantity has been called **unit charge of the ion** A univalent ion thus carries one charge of *electricity* (96,540 coulombs), a bivalent ion two charges, and an *n* valent ion, *n* charges According to this view, valency represents the number of charges of electricity which are associated with the respective ions, and **chemically equivalent quantities of matter have the same capacity for electricity. The chemical equivalent is the electrical unit of** *matter*, or, as Faraday expressed it

The equivalent weights of bodies are simply those quantities which contain equal quantities of electricity, or have naturally equal electric powers, it being electricity which determines the *equivalent number*, because it determines the combining force Or, if we adopt the atomic theory or phraseology, then the atoms of bodies which are equivalent to each other in their ordinary chemical action have equal quantities of electricity naturally associated with them.

Berzelius' dualistic theory—According to J J Berzelius (1812) each element possesses a definite quantity of positive or negative electricity as an integral part of its constitution, and "every chemical action is fundamentally an electrical phenomenon," and "electricity is the first cause of all chemical activity" The varying degrees of chemical affinity were *supposed* to imply that the different substances were charged with *varying quantities* of electricity When, say, sodium unites with oxygen to form the base sodium oxide, Na_2O, and sulphur with oxygen to form the acid anhydride sulphur trioxide, SO_3, primary compounds or compounds of the first order are formed But the electrical attractions were not supposed to be always neutralized during the formation of these primary compounds, for the excess of positive or negative electricity caused a further attraction between the acidic and basic radicles, and resulted in the formation of compounds of higher orders

The dualistic theory reigned supreme in chemistry for many years, but it was practically abandoned when Avogadro's hypothesis was generally accepted, because Berzelius' theory was incompatible with such a comparatively simple reaction as $2H_2 + O_2 = 2H_2O$ According to Berzelius, the compound nature of oxygen is due to different electrical charges on the component atoms of the molecule This does not agree with the supposed identity of the resulting two molecules of water, H_2O Again, J B Dumas (1834) showed that the hydrogen atoms in compounds like CH_4 can be replaced one by one by atoms of chlorine J J Berzelius had postulated that hydrogen is an electro positive element, and chlorine electro negative as exemplified in hydrogen chloride Here, in Dumas' substitutions, a negative element can be exchanged for a positive element without fundamentally altering the chemical character of the resulting compounds Facts like these brought Berzelius' theory into disfavour

Faraday often expressed his conviction that "the forces termed chemical affinity and electricity are one and the same", and that "chemical affinity is a consequence of the electrical attractions of particles of different kinds of matter" Contrary to Berzelius' assumption, Faraday proved that on electrolysis *definite and fixed quantities* of electricity are associated with the atoms of matter, although atoms of the same kind of matter in different compounds, on electrolysis, might be charged with different yet definite quantities of positive or of negative electricity These statements are not antagonistic to "the kinetic theory of atoms" (p 121).

§ 3 The Velocity of Electrolytic Conduction

An electric current travels through an electrolytic solution as quickly as if the same current were sent through a copper wire of the same resistance, and the products of electrolysis appear simultaneously at both electrodes however far apart the electrodes be placed N M Hopkins (1905) passed a current through a tube 1500 cm long, and through another tube 10 cm long, and measured the time required for the current to pass by means of a chronograph sensitive to nearly 10,000 cm per second The tubes were filled with dilute sulphuric acid and fitted with electrodes—the anode of copper, and the cathode of platinum As soon as the current passes, bubbles of hydrogen appear at the cathode simultaneously with the blue colour of copper sulphate at the anode The electrolyte 1500 cm

long conducted as quickly as an electrolyte 10 cm long The experiment can be illustrated by the apparatus sketched in Fig 125, which almost explains itself The long spiral tube contains the electrolyte as in Hopkins' experiment As soon as the circuit is closed, electrolysis begins

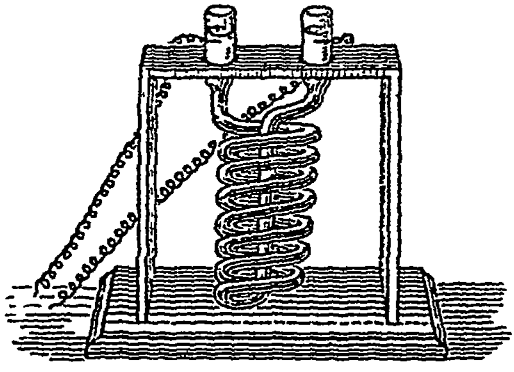


Fig 125 —Velocity of Electrolytic Conduction.

The known rates of diffusion of molecules in solutions are altogether too slow to allow the SO_4 which attacked the copper, to have come from the same H_2SO_4 molecule as the hydrogen liberated at the cathode Further, it is supposed that the electrical energy used in electrolysis is entirely expended in overcoming the resistance of the electrolyte, and no measurable quantity of work is needed for tearing apart the components of the decomposing molecule Hence it follows that the molecules of an electrolyte in solution must be in a condition to conduct the electric current immediately the necessary electrical stress is applied to overcome the resistance of the liquid

§ 4 The Effect of the Solvent

The more care taken in the purification of water, the less does it conduct electricity, and consequently, it is assumed that pure water is a non-conductor in spite of the fact that perfectly non conducting water has not yet been made Pure dry liquid hydrogen chloride, like water appears to be a non conductor A mixture of water and hydrogen chloride is an electrolyte Hence it is inferred that the electrolytic conductivity of a solution is a property of solvent and solute, and not a property of either constituent alone Solutions of dry hydrogen chloride in some solvents —e.g dry benzene or chloroform—do not conduct electricity, and solutions of some substances in water conduct no better than water itself—e g. solutions of sugar or alcohol in water Hence also, it follows the electrolytic conductivity of a solution depends upon some specific relation between the solvent and the *solute* In a general way, aqueous solutions of acids, bases, and salts conduct electricity, and these substances are often called electrolytes, not because the salt conducts the current, but because their aqueous solutions conduct the current electrolytically Some fused salts—*e g* silver chloride—conduct electrolytically.

§ 5 The Ionic Hypothesis

Let us learn to dream, then perhaps we shall find *the truth* —A KEKULÉ

The main facts so far established by our discussion of the phenomena attending electrolysis may now be summarized

(1) Electrolytes in solution conduct electricity, and the process of electrical conduction is attended by a splitting of the molecules

of the solute into anions and cations, the anions appear at the anode, and the cations at the cathode The separation of a certain number of anions at the anode is simultaneously attended by the separation of a chemically or electrically equivalent number of cations at the cathode During electro lysis, the anions and cations appear to be discharged electrically, because electrically neutral molecules appear as secondary products of the electrolysis

(2) The anion which separates at the anode is not necessarily derived from the same molecule as the cation which appears at the cathode

(3) Solvent and solute together make a conducting medium, since as a rule neither solvent nor solute alone shows a marked capacity for conducting electricity

(4) No measurable time is needed to put an aqueous solution in a condition to conduct the current Immediately, the necessary difference of potential appears at the electrodes the process of electrolysis begins

(5) Osmotic pressure and related phenomena show that electrolytes in dilute solution have what seems to be a molecular weight which suggests that the "ordinary" molecule of a solute in certain solvents is dissociated into two parts

As a trial hypothesis it may be assumed that the mere presence of the solvent leads to the fission of the molecules of the electrolyte into sub molecules, each of which is charged with a definite amount of positive or negative electricity equivalent to 96,540 coulombs per chemical equivalent The solution does not itself appear to be electrically charged, and hence it is assumed that equal quantities of positive and negative electricity are developed by the rupture of the molecules of the electrolyte during the process of solution Solutions of electrolytes are supposed to normally contain a definite proportion of the sub-molecules charged with electricity By a modification of Faraday's definitions (p 24), the "sub molecules" are called ions, and consequently **ions are atoms or groups of atoms which carry a positive or negative charge of electricity, and they are formed by the dissociation of the electrolyte in the solution Each molecule, on dissociation, furnishes two kinds of ions with equal and opposite charges of electricity** To avoid confusing the phenomenon of dissociation in which the products are not charged electrically, with the dissociation of a molecule into electrically charged ions, the term ionization is reserved for the latter phenomenon The ionization of hydro chloric acid is represented in symbols $HCl \rightleftharpoons H^{\cdot} + Cl'$, and of sodium chloride $NaCl \rightleftharpoons Na^{\cdot} + Cl'$ This startling hypothesis appears so incredible and so opposed to the instinct, "common sense," or prejudices of the chemist that it has been assailed by much wholesome criticism—particularly by H. E Armstrong For instance, it is asked

1 *In view of the great chemical activity of metallic sodium in contact with water, is it profitable to postulate the existence of the element sodium in contact with water without chemical action?* This objection is said to "rest on a misunderstanding," because *electrically charged ions* of sodium in an aqueous solution of sodium chloride are very different from *neutral atoms* of metallic sodium The ions of sodium carry large charges of electricity

It is urged that "chemists know practically nothing about the properties of atoms carrying large charges of electrical energy," and also that "the chemical activity of an atom of sodium charged with its 96,540 coulombs of electricity is much less than a neutral atom of sodium" In other words, the presence of the electrical charge on the sodium ion keeps the ordinary chemical activities of the atom in abeyance This means that whenever a chemical difficulty arises in the application of the ionic hypothesis the assumption is made that "neutral atoms or atomic groups and ions are different substances," because the properties of a substance are determined as much by the energy it contains as by the kind of matter In this way, the ions have been invested with such imaginary properties as may be needed to keep the ionic hypothesis consistent with facts

2 *Bodies carrying electrical charges of opposite sign are attracted and cling to one another, if therefore a mobile solution contains "free and independent" ions carrying enormous electrical charges of opposite sign, how can the charged ions remain more than momentarily free?* It is assumed that a certain proportion of the molecules of the solute are continually breaking down into free (charged) ions, and a certain proportion of the ions are continually recombining to form ordinary molecules, the result is, that the ratio between the number of free ions and paired ions (molecules) remains unchanged. This statement, of course, does not answer the perplexing question Attempts have been made to refer the difficulty to the specific insulating properties of the solvent The action of the solvent has been compared with the function of the glass in a charged Leyden jar This agrees with the non conducting qualities of pure water, but experiments have shown that the relation between the insulating properties of a solvent and its ionizing properties is not an adequate and sufficient explanation of the observed facts The two phenomena do not always vary concomitantly A satisfactory answer to the question, therefore, has not yet been found

3 *If an ionized salt, say, sodium chloride, is present in solution as a mixture of Na and Cl' ions, it might be thought possible to separate the two components by diffusion or by some other mechanical process* S Arrhenius answers that the great electrostatic attraction of the oppositely charged ions prevents any marked diffusion W Nernst, however, has shown that the concentration currents produced when, say, a solution of sodium chloride is carefully covered with a layer of water, leads to the conclusion that the greater mobility of the chlorine ions charges the upper layer negatively, and the lower layer positively, so that a current of electricity can be obtained by placing the two layers in electrical contact —See "Concentration cells"

4 *When a compound is formed from its elements with the loss of energy, the compound cannot be resolved into its elements unless energy be supplied It is therefore pertinent to inquire What is the source of the energy which leads to the fission of the molecule into ions carrying equal but opposite charges of electricity?* Here, again, it is necessary to reiterate that the ionic hypothesis refers not to the separation of a compound into its original constituents, but into charged ions, and it is interesting to observe that molecules of sodium chloride, etc, which appear to be very stable when dry, react with great facility when in solution A little heat is supposed to be evolved during the ionization of many (not all) electrolytes, and the

process of ionization is then presumably accompanied by an exothermal reaction which more than compensates for the energy needed for the fission of the molecule into oppositely charged ions J D van der Waals (1891) expressed the idea that ionization is primarily due to the affinity of ions for the solvent, and that the heat of hydration of the ions furnishes the energy needed for the ionization of the salt To this, D Konowalow (1893) adds, "only those solvents which react chemically with the solute furnish solutions which conduct electricity"

These answers, based on circumstantial evidence, are not altogether satisfactory, but they have made it almost certain that if ions are formed at all, the ions do not usually exist alone in the solution, but that each ion forms a complex by association with a definite number of molecules of the solvent The ionic theory primarily assumes that the apparent *number* of solute "molecules" is increased by ionization, and it makes very little difference to the applications of the ionic theory whether it be assumed that each ion is isolated as a distinct individual, or whether each ion forms a complex with the molecules of the solvent The number of ions is the same in both cases The explanation of the phenomena, particularly when solutions other than water are considered, is beset with many difficulties on account of the unknown relations between the solvent and solute So much is this the case that M. le Blanc (1907) considered "it to be very fortunate for the advance of electro chemistry that such complications are generally, though not always, absent in the case of aqueous solutions. It is due to this fact that it has been possible to deduce simple laws from the study of aqueous solutions"

Several attempts have been made to work out a consistent explanation of the fundamental facts without a theory of charged ions, but with hypotheses based upon the formation of imaginary molecular complexes by a reaction between polymerized solvent and the molecules of the solute. The difficulties, however, are discussed in special text-books

These controversial matters are mentioned in this elementary book to emphasize the fact that an explanation of a phenomenon may contain part of the truth, and yet not "the whole truth, and nothing but the truth." In that case, we try the hypothesis by the test indicated in the first chapter, and ask Is the hypothesis useful? The answer is that the ionic hypothesis has done good work, and it promises to do more An hypothesis is not always to be discarded as a first approximation, because troublesome exceptions crop up from time to time Newton's theory of gravitation, for instance, appeared to be afflicted with such blemishes—particularly in its early days, so was the theory of opposing reactions once considered to be unreasonable folly In spite of important difficulties, we shall now try how the ionic hypothesis fits in with a few important phenomena.

History—R Clausius (1857) first suggested that the molecules of a solute are ionized when dissolved in the solvent, but Clausius appears to have had some "chemical" misgivings, for he added that the ionization only affected an infinitesimally small fraction of the total number of dissolved molecules. As the ions are discharged at the electrodes during electrolysis, more molecules are ionized The un-ionized molecules keep the electrolyte constantly supplied with a definite number of ions. The ions conduct the current, the "undissociated" molecules are inactive Further, at any given temperature, there is a constant relation between the number

of unionized molecules, and the number of ions W Giese (1882), and S Arrhenius (1884), more bold, or less cautious, than Clausius, asserted that a considerable fraction of the dissolved molecules are ionized, and that the number of ions increases more and more as the solution becomes more and more dilute W Ostwald, J H van't Hoff, W Nernst, and a large number of other workers have followed the logical consequences of Arrhenius' hypothesis in a great many directions, the results, on the whole, have been satisfactory, and the theory has thus stimulated the study of the properties of solutions in a remarkable manner Some hold that the "principle of exhausting hypotheses," indicated on p 7, has not been followed, and that the favoured child—the ionic hypothesis—has grown into a tyrannical master, for instance, G F Fitzgerald (1896) has said that "the supposed advantage of the free ion theory is not only illusory but misleading" If this be a correct diagnosis of the ionic hypothesis, we have some consolation in the fact "The destruction of an error hardly ever takes place without the discovery of truth" (H Davy, 1810)

§ 6 The Number of Ions in a Solution.

The process of electrolysis, according to the ionic hypothesis, is supposed to proceed somewhat as follows There is a constant difference of potential between the poles of a battery, and if the poles are put in communication, the electricity is immediately discharged The battery at once reproduces the same difference of potential as before by generating more electricity Again, when a salt—say, sodium chloride—is dissolved in water, some of the dissolved molecules are, by hypothesis, ionized, and the ions immediately begin to recombine to form molecules The speeds of the two reactions are supposed to behave analogous with opposing reactions, and a state of equilibrium is reached when the number of molecules reformed by the combination of the ions is equal to the number of molecules ionized in the same time

Still further, when the two poles of a battery—say platinum electrodes —are dipped in the salt solution as indicated in Fig 5, all the chlorine ions, carrying a negative charge, are attracted to the anode or positively charged electrode, and the positively charged sodium ions are attracted to the cathode or negatively charged electrode As each ion comes in contact with the electrode with a charge of opposite sign to its own, the ion is relieved of its charge, and thereby reverts to an ordinary atom of chlorine or sodium The chlorine atoms, being unable to attack the water or the electrode, unite in pairs to form molecules of chlorine gas As soon as the liquid in the vicinity of the anode is saturated with chlorine, this gas bubbles to the surface of the liquid Similarly, the sodium ions are relieved from their charges at the cathode, and the resulting sodium atoms immediately attack the water, forming hydrogen gas and sodium hydroxide $2Na + 2H_2O = 2NaOH + H_2$, the hydrogen bubbles off as a gas

The equilibrium between the unionized molecules and the ions is disturbed by the annihilation, so to speak, or the removal of ions at the electrodes The difference of potential at the electrodes is maintained by the battery, and the supply of ions is kept up by the steady ionization of the salt as fast as the ions are de electrified at the electrodes, until practically

the whole of the salt in the solution has been electrolyzed. Thus, it has been said that "the ions do not transport the electricity of the battery, but their own" The charged ions are already present in the solution before connection is made with the battery

If water be progressively added to an aqueous solution of sodium chloride, containing, say, one gram-molecule (58 5 grams) per litre, at 18°, the electrical conductivity of the solution increases until a certain limit is reached Subsequent additions of water have no further influence on the conductivity of the solution This is illustrated by the curve, Fig 126, which represents the rapid rise in the conductivity of sodium chloride solutions with decreasing concentration, the conductivity reaches a maximum very quickly when further additions of water have no further influence on the result Hence the conductivity of an electrolytic solution increases with dilution, reaches a maximum value approximately corresponding with infinite dilution When the dilution has reached the limit beyond which no further increase in the conductivity can be observed, it is supposed that the salt is all ionized, and no more ions can be supplied by the solute, however much more solvent be added All the ions which can be obtained from the solute take part in conducting the electric current at infinite dilution

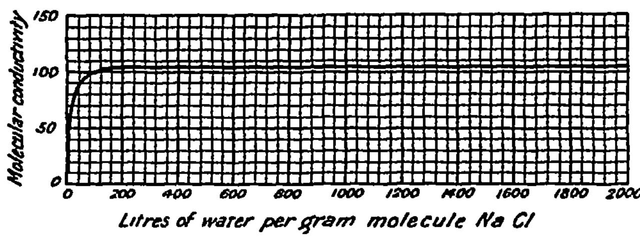


FIG 126 —Effect of Concentration on the Conductivity of Aqueous Solutions of Sodium Chloride

Usually, the conductivity of a solution is measured indirectly The resistance which the solution offers to the passage of a current is directly measured It is more convenient to take the reciprocal of the resistance and call it the conductivity of the solution. The specific resistance is first determined, that is, the resistance which is equivalent to the resistance of a cubical mass of the solution whose length of side is 1 cm From this, the so called equivalent conductivity is calculated The equivalent conductivity of a substance represents the conducting power of one gram equivalent of the substance dissolved in the solvent, and placed in a cell whose opposite walls, one centimetre apart, form the electrodes Otherwise expressed, the equivalent conductivity represents the conducting power of a layer of the solution 1 cm thick, and containing one gram-equivalent of the substance in solution If the conductivity be referred to a gram molecule, and not a gram-equivalent, it is termed the molecular conductivity of the solution

It is now assumed that the number of ions which take part in conducting the electric current at any particular concentration of the solution is proportional to the conductivity, λ, of the solution Consequently, if x represents the fraction of a gram molecule which is dissociated into ions when the solution occupies v litres, we have, at dilution v, the conductivity—$\lambda_v = kx$, where k is the constant of proportion At infinite dilution, the whole gram-molecule is supposed to be ionized, and consequently, $x = 1$, and therefore the conductivity, λ_∞, at infinite dilution, is $\lambda_\infty = k$ Substitute this value of k in the preceding equation, and we get

$$x = \frac{\lambda_v}{\lambda_\infty}$$

which, by hypothesis, means that the fractional number of molecules ionized in a solution is numerically equal to the equivalent conductivity of the solution divided by the equivalent conductivity of the solution at infinite dilution, or,

$$\text{Degree of ionization} = \frac{\text{Number of molecules ionized}}{\text{Total number of molecules}} = \frac{\lambda_v}{\lambda_\infty}$$

The above formula enables the electrical conductivity of a salt to be expressed in terms of the degree of ionization of the salt in solution Thus, the equivalent conductivity of a solution of hydrochloric acid is 305 4, and the same acid at infinite dilution has the equivalent conductivity 349 3 Hence the degree of ionization is 305 4 — 349 3 = 0 874 per gram molecule, or 87 4 per cent ionization. This means that 12 6 per cent of the molecules in the solution are present as unionized neutral molecules, HCl, and 87 4 per cent of the molecules are present in the ionic form H + Cl′ Or,

$$\underbrace{\text{HCl}}_{\text{12 6 per cent}} \rightleftharpoons \underbrace{\text{H} + \text{Cl}'}_{\text{87 4 per cent}}$$

The *percentage ionization* must not be confused with the *absolute concentration of the ions* The former may be the greater in dilute solutions, and the latter greater in concentrated solutions The ionic hypothesis thus assumes that an aqueous solution of hydrochloric acid contains three distinct kinds of "solute molecules," electrically charged molecules (hydrogen and chlorine ions), and neutral hydrogen chloride molecules

Table XVI shows the degree of ionization of a few typical acids, bases, and salts selected merely for illustrative purposes

TABLE XVI —DEGREE OF IONIZATION OF SOME TYPICAL ACIDS, BASES, AND SALTS.

ACIDS		BASES		SALTS	
Acid	% ionized	Base	% ionized	Salt	% ionized
Nitric acid (62 %)	0 096	Potassium hydroxide	0 77	Potassium chloride	0 74
Nitric acid (dil)	0 820	Sodium hydroxide	0 73	Ammonium chloride	0 75
Sulphuric acid (dil)	0 510	Lithium hydroxide	0 63	Potassium nitrate	0 64
Carbonic acid ($\frac{1}{10}$ N)	0 0017	Ammonium hydroxide	0 005	Zinc sulphate	0 24
Hydrosulphuric acid ($\frac{1}{10}$ N)	0 0007	Calcium hydroxide ($\frac{1}{64}$ N)	0 90	Copper sulphate	0 22
Perchloric acid ($\frac{1}{2}$ N)	0 880	Barium hydroxide ($\frac{1}{64}$ N)	0 92	Silver nitrate	0 58

The effect of increasing the concentration of a solution is to increase the internal friction This retards the movements of the ions and thus diminishes the conductivity more rapidly than would occur if the results were not affected by this disturbing factor As the concentration decreases, the friction diminishes, and, with the more dilute solutions, the effects of internal friction can be neglected The two factors—internal friction and conductivity—do not change with dilution in the same way,

and, in consequence, the conductivity may increase with increasing dilution, reach a maximum, and then decrease with increasing dilution This is the case, for instance, with sulphuric acid, where the maximum conductivity occurs when 30 per cent of acid is present The application of the ion theory to *concentrated* solutions is beset with many difficulties, and consequently the theory has been mainly developed from results obtained with *dilute* solutions Similar remarks apply to solvents other than water

Illustration of the different conductivities of electrolytes—The difference in the conductivity of, say, hydrochloric, sulphuric, chloracetic, and acetic acids, containing $\frac{1}{50}$ gram-equivalent of the respective acids per litre, is well shown by W R Whitney's apparatus (1900), illustrated in Fig 127 Electrodes are fixed in four vertical tubes The upper electrodes are connected with one terminal (as shown by the dotted line), which is connected with the lighting circuit Each of the lower electrodes is connected with one terminal of an ordinary incandescent lamp The other terminals of the lamps are connected with another terminal which is connected with the lighting circuit (say an alternating current, 110-volt) The upper electrodes can be moved up or down, the lower electrodes are fixed The tubes are filled with the four acids just indicated, and the electrodes are adjusted the same distance apart. The current is switched on The lamp connected with the hydrochloric acid tube glows brightest, that with the sulphuric acid comes next, the chloracetic acid next, and the one connected with the acetic acid tube scarcely glows at all The electrodes can now be adjusted until the lamps all glow equally bright It will be found that the distances between the electrodes are approximately as 100 85 15 1 when the acids are arranged in the order named above These numbers give an approximate measure of the conductivity of these acids, and also, by hypothesis, of their degrees of ionization

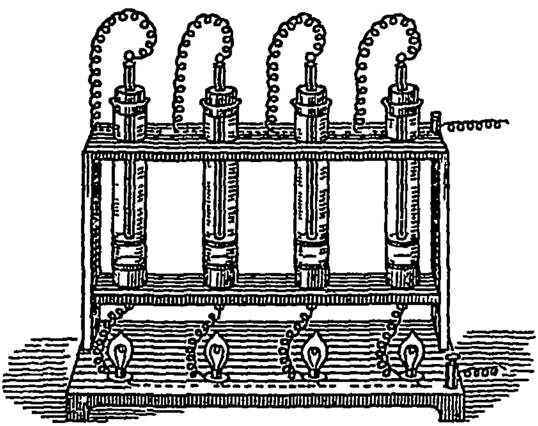


FIG 127 – Different Conductivities of some Acids

Strong and weak acids and bases—The terms "strong" and "weak" are sometimes applied to the acids and bases, and these terms refer to the conductivity or the degree of ionization in aqueous solution of moderate dilution There is no real line of demarcation between the two Acids like carbonic and hydrosulphuric acids, and bases like ammonia, are weak Their degree of ionization is less than one per cent If the degree of ionization exceeds 70 per cent the acid is undoubtedly strong[1] Most of the salts are highly ionized, even at moderate dilutions, but there are

[1] Electrolytes like solutions of sodium chloride are good conductors, and some solutions with a conductivity midway between good conductors and non conductors are sometimes called semi or half electrolytes.

many exceptions, *e g* mercuric chloride, the cadmium halides and mercuric cyanide are but slightly ionized in moderately dilute solutions

§ 7 The Migration of Ions

Mix a hot 5–10 per cent aqueous solution of gelatine with a little cupric chloride solution, and pour the blue solution, while hot, into a warm U tube with long legs until the U-tube is a little over half full Take care to introduce as few air bubbles as possible Let the mixture solidify by cooling When cold, slip a rubber ring over each leg of the tube so as to mark the level of the gelatine in each leg Pour a dilute solution of sodium chloride into each leg, dip a piece of platinum wire into the solution of sodium chloride, and pass a current of electricity through the contents of the U-tube while the latter is immersed in a freezing mixture,[1] Fig 128, to prevent the softening of the gelatine during the passage of the current The gelatine simply serves to prevent mechanical movements of the liquid during the passage of the current The presence of the gelatine does not otherwise interfere with the electrolysis The experiment is more interesting if a second U-tube be prepared with potassium dichromate in place of copper chloride, and connected in series with the copper chloride tube as indicated in Fig 128 A current of electricity is then passed through the tubes *viâ* the platinum wire electrodes, each of which dips in a dilute solution of sodium chloride above the gelatine After the current has passed some time, the blue solution rises past the level of the solid gelatine towards the cathode, and descends below the level of the gelatine on the anode side The gelatine has not moved, and it appears as if the current "drives" the copper chloride molecules towards the cathode, the movements in the other tube are in the converse direction, so that it appears as if the current "pulls" the molecules of the potassium dichromate towards the anode One tube with copper dichromate can be used in place of copper chloride and potassium dichromate The gelatine is green, but a blue coloration rises towards the cathode, and a yellow coloration rises towards the anode

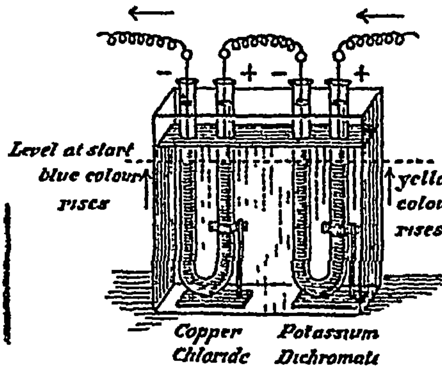


FIG 128 —Migration of Ions to the Electrodes

The ionic theory interprets these experiments of A A Noyes and A A. Blanchard (1900), by assuming that in the case of cupric chloride, blue copper ions travel towards the cathode and colourless chlorine ions towards the anode, in the second experiment, that yellowish Cr_2O_7-ions travel towards the anode and colourless potassium ions towards the cathode, and in the third experiment, blue copper ions travel towards the cathode and yellow dichromate ions towards the anode The fact observed is that the electrolysis of the coloured solutions occurs at the boundary surfaces between the gelatine and the supernatant solution

By a modification of these experiments, it is possible to measure the rates at which the concentration of the solution changes about the electrodes, or, in the language of the ionic theory, the rates at which the anions of copper, etc., drift towards the electrodes For example, if a solution of silver nitrate of known concentration be electrolyzed between silver electrodes in an apparatus similar to that illustrated in Fig 129, the only change in the solution is a transfer of silver from the anode to the cathode,

[1] Say, ammonium nitrate and cold water

and a change in the concentration of the silver salt round the two electrodes, for the apparatus is constructed so as to reduce the mechanical convection of the dissolved salt to a minimum The change in the concentration of the solution, after a few hours' electrolysis can be measured by withdrawing about half the solution from the apparatus, *via* the stopcock, and determining the amount of silver in the solution by analysis From the results numbers can be obtained which are supposed to represent the speeds of migration of the *anions and the cations* *The following numbers, due to* W Hittorf (1853), serve to illustrate the principle

Hittorf's experiment — A solution of silver nitrate containing one part of silver to 19 44 parts of water was electrolyzed for nearly an hour in a cell with silver electrodes Silver dissolved from the anode and a similar quantity deposited on the cathode The concentration of the whole solution remained unchanged, but the concentration of the solution about the cathode decreased while that about the anode increased In the cathode compartment, Hittorf found

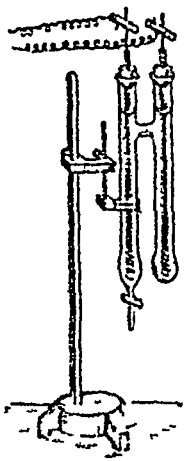


FIG 129 —Determination of the Speed of Ionic Migration

Silver before electrolysis	0 7162	gram
Silver after electrolysis	0 5862	"
Loss	0·1300	"

The solution about the cathode thus lost 0 1300 gram of silver, and the solution about the anode must have increased by this amount owing to the action of an equivalent quantity of nitric acid on the silver electrode At the same time, by the simultaneous interposition of a silver voltameter in the circuit, it was found that sufficient electricity had passed through the electrolyte to deposit 0 2470 gram of silver at the cathode If no silver ions had passed from the anode chamber, the quantity of silver in the anode chamber would have increased by 0 2470 gram owing to the migration of NO_3' ions from the cathode chamber The observed increase was only 0 1300 gram of silver, hence 0 2470 less 0 1300 gram, in all, 0 1170 gram of Ag ions migrated from the anode chamber to the cathode chamber, while the cathode chamber simultaneously lost 0 1300 gram of silver due to the deposition of 0 2470 gram of silver on the cathode Hence since the relative speeds of the ions are proportional to the fall of the concentration about the oppositely named electrodes,

$$\frac{\text{Loss in cathode chamber}}{\text{Loss in anode chamber}} = \frac{0\ 1300}{0\ 1170} = \frac{\text{Speed of anion } NO_3'}{\text{Speed of cation, Ag}}$$

Or the rate of migration of the anions is to the rate of migration of the cations as 130 117, or the NO_3' ions migrate 1 1 times as fast as the Ag ions

By measuring the rate of rise of the blue colour in the experiment Fig 128, the absolute velocity of copper ions can be determined under standard conditions and in that way, with other solutions, a series of numbers have been obtained which are called the **transport numbers** or the **speeds of migration** of the different ions The speed of migration so defined is a specific property of each ion and is independent of the other ions present The speeds are increased by using currents of greater

electromotive force At 18°, with a difference of potential of one volt between the electrodes, the speeds of migration of some ions are

Anions	OH'	Cl'	I'	NO_3'	
Speeds	5 6	2 12	2 19	1 91	cm per hour
Cations	Cs	Rb	K	Na	Li
Speeds	2 32	2 32	2 05	1 26	1 11 cm per hour

The heaviest ions, that is, the ions with the greatest "atomic" weights, here appear to move fastest This has been supposed to be due to the slower moving ions dragging along with them a number of molecules of the solvent

In these experiments the *fact* observed is the changing molecular concentration of the solution about the anode and cathode during electrolysis, the extraordinary *hypothesis* is that during the passage of the current the anions and cations move in the same electrolyte with different velocities and yet the anions and cations are given off at the respective electrodes at the same time!

§ 8 "Abnormal" Osmotic Pressures and Ionization

We are now in a position to resume our study of the abnormal osmotic pressures furnished by solutions of electrolytes Suppose that one molecule of an electrolyte furnishes m ions and further let x denote the fraction ionized when a gram-molecule of the electrolyte is dissolved in water The solution will then contain $(1 - x)$ non-ionized molecules, and mx ions. The total number of individual molecules in the solution—that is, electrically charged molecules (ions) and neutral molecules—will be $(1 - x) + mx$ As in our previous study of solutions, let n denote the total number of individual molecules formed by the ionization of a substance in a given solution Then $n = 1 + mx - x$ The numerical value of n, as we have seen, can be determined from conductivity data, and from osmotic pressure and related phenomena—freezing and boiling point determinations If the value of n so determined be divided by the value of n calculated on the assumption that no ionization occurs, the value of x and accordingly also the value of n can be computed For example, the solution of hydrochloric acid just studied gives $x = 0\ 874$, and $m = 2$ Hence $n = 1 + (m - 1)x$ becomes $n = 1\ 874$ Hence every 100 molecules of HCl furnish 187 4 individual molecules. If the electrolyte had been non-ionized, n would have been unity, and if completely ionized, n would have been 2

A comparison of the values of n calculated from osmotic pressure, freezing point, and electrical conductivity data is indicated in Table XVII

The numbers in the last three columns show that the values determined by independent processes are strikingly concordant; and it is therefore inferred that the abnormal osmotic pressures indicated in Table VIII, p 222, arise from the more or less complete ionization of the electrolytes in aqueous solution

Modes of ionization —The ionization of some of the multivalent electrolytes—H_2CO_3, H_2SO_4 $BaCl_2$, $CdCl_2$, K_2SO_4, $CuSO_4$, etc —in moderately dilute solutions appears to furnish complex ions Thus, cadmium chloride, $CdCl_2$, not only

furnishes $Cd^{\cdot\cdot} + 2Cl'$, but also $Cd^{\cdot\cdot} + CdCl_4''$, sulphuric acid, H_2SO_4, not only gives $2H^{\cdot} + SO_4''$, but also $H^{\cdot} + HSO_4'$, carbonic acid, H_2CO_3, gives $2H^{\cdot} + CO_3''$, and $H^{\cdot} + HCO_3'$, copper sulphate, $CuSO_4$, not only gives $Cu^{\cdot\cdot} + SO_4''$, but also $Cu_2SO_4^{\cdot\cdot}$ and $Cu(SO_4)_2''$, etc If, however, the solutions be still further diluted, the complex ions break down into simpler ones Hence the ionization of concentrated polybasic acid like H_2SO_4 proceeds in stages first $H_2SO_4 = H^{\cdot} + HSO_4'$, followed by $H^{\cdot} + HSO_4' = 2H^{\cdot} + SO_4''$

TABLE XVII —MOLECULAR WEIGHTS OF SOME ELECTROLYTES IN SOLUTION

Salts	Molecular concentration	Values of n		
		Osmotic pressure	Freezing point	Conductivity
Calcium nitrate $Ca(NO_3)_2$	0 18	2 48	2 47	2 46
Magnesium sulphate, $MgSO_4$	0 38	1 25	1 20	1 35
Strontium chloride, $SrCl_2$	0 18	2 69	2 52	2 51
Potassium chloride KCl	0 14	1 81	1 86	1 86
Lithium chloride, $LiCl$	0 13	1 92	1 94	1 84
Magnesium chloride, $MgCl_2$	0 19	2 79	2 68	2 48

§ 9 Equilibrium between Ionized and Non-ionized Solute

Reference has previously been made to the assumption that the molecules of an electrolyte, when dissolved in water, are ionized, that the ions, at the same time, recombine to form neutral molecules, and that equilibrium will ensue when the speeds of the two opposing reactions—ionization and de ionization—are equal Consider the ionization of ammonium hydroxide, NH_4OH, represented by

$$NH_4OH \rightleftharpoons NH_4^{\cdot} + OH'$$

Here the process of ionization bears some analogy with the dissociation of iodine by heat $I_2 = I + I$ Let $[NH_4OH]$ denote the concentration of the ammonium hydroxide, $[NH_4^{\cdot}]$ the concentration of the ammonium ion, and $[OH']$ the concentration of the hydroxide ion Then, applying the principle of opposing reactions, the condition for equilibrium is

$$\frac{[NH_4^{\cdot}] \times [OH']}{[NH_4OH]} = K$$

If this theory applies to ions, the numerical value of the equilibrium constant, now called the **ionization constant**, remains unchanged whatever be the concentration of the solution This principle is sometimes called **W Ostwald's dilution law**

EXAMPLE —In a solution containing 0 125 gram molecules of NH_4OH per litre, the equivalent conductivity shows that 0 0135 gram molecules are ionized, and hence, $0{\cdot}0135 \times 0\ 125 = 0\ 0017$ represents the molecular concentration of the ammonium hydroxide which is ionized This number thus represents the concentration of the $NH_4^{\cdot}$ ions But every $NH_4^{\cdot}$ ion is accompanied by one OH' ion, and accordingly $0{\cdot}0017$ also represents the concentration of both the $NH_4^{\cdot}$ and the OH' ions Hence, from Ostwald's dilution law, $0\ 0017 \times 0{\cdot}0017 \div (0\ 125 - 0\ 0017) = 0\ 000023$ This last number represents the value of the ionization constant for a $\frac{1}{8}$ normal solution of ammonium hydroxide

If the solution be diluted, the *percentage amount* of ionization increases (although, of course, the *actual* concentration of the ions must decrease), and with more concentrated solutions, the percentage amount of ionization decreases. Table XVIII represents values for the ionization constant for solutions of ammonium hydroxide of different strength

TABLE XVIII.—EFFECT OF DILUTION ON THE IONIZATION OF AQUEOUS AMMONIA

Ammonium hydroxide (Gram-molecules per litre.)	Proportion ionized	Molecular concentration of NH_4 and of OH' ions (Gram "ions" per litre.)	Molecular concentration of non-ionized NH_4OH (Gram-molecules per litre.)	K
1 0000	0 0047	0 0047	1 0000–0 0047	0 000023
0·1250	0 0135	0 0017	0 1250–0 0017	0 000023
0 0159	0·0376	0 0006	0 0159–0 0006	0 000023
0 0039	0 0754	0 0003	0 0039–0 0003	0 000023

The constancy in the value of K means that although the last named solution of ammonium hydroxide is nearly 300 times more dilute than that named first, and the degree of ionization of the last is nearly 16 times as great as the first, the expression represented by K, deduced on the supposition that the process of ionization follows the rule for opposing reactions, is constant within the limits of experimental error

When this method is applied to strong acids and bases, that is, acids and bases more highly ionized than ammonium hydroxide—the results are not nearly so good, and the most satisfactory explanation of the discrepancy turns on the assumption that the dissolved substance unites with the solvent so that in the more concentrated solutions part of the liquid in which the substance is dissolved no longer functions as a solvent because it is in combination with ions and non ionized molecules of the solute This assumption is at the base of the solvate theory of solutions advocated by H C Jones

§ 10. The Solubility Law.

In the case of an aqueous solution of sodium chloride, containing, say, 58 5 grams, that is, one gram molecule per litre, we have $NaCl \rightleftharpoons Na + Cl'$, where 68 per cent of the salt is ionized The condition of equilibrium, according to the dilution law, is

$$\frac{[Na][Cl']}{[NaCl]} = K, \quad \frac{0\ 68 \times 0\ 68}{0\ 32} = 1\ 44 = K$$

If either Na or Cl' ions be added[1] to the solution—say, hydrogen chloride—making the concentration of the Cl' ions 0 75 instead of 0 68—then, in order to preserve the constancy of the ratio 1 44, the concentration of the Na ions must be diminished This can only occur by the union of some Na and Cl' ions to form NaCl until the ratio K is again 1 44

Solubility of mixtures with a common ion —*Sodium chloride is in* equilibrium with its aqueous solution when, at a given temperature, the

[1] If Cl' ions be added, they must necessarily be accompanied by an equivalent number of oppositely charged ions of, say, K, from, say, a solution of potassium chloride, or of Na' ions from, say, sodium hydroxide $NaOH \rightleftharpoons Na + OH'$

concentration of the substance in solution has a certain definite and constant value—the solubility of the substance at the given temperature. Since the sodium chloride in solution is partly ionized, there are two equilibria to consider, first, the relation between the non-ionized and the ionized salt in solution $NaCl \rightleftharpoons Na^{\cdot} + Cl'$ just indicated, and second, the relation between the non ionized salt and the solid. If the solution be saturated, we have

$$NaCl_{solid} \rightleftharpoons NaCl_{solution} \rightleftharpoons Na^{\cdot} + Cl'$$

If the concentration of the $Na^{\cdot}$ or the Cl' ions be augmented, some of the $Na^{\cdot}$ and Cl' ions will recombine to form non-ionized NaCl as indicated above. Consequently, some sodium chloride will be precipitated or the solution will be supersaturated. **Hence the solubility of a salt is usually diminished in the presence of another compound with a common ion.** If the solution of the hydrochloric acid had been isohydric with the salt solution—*i e* if the number of chlorine ions per cubic centimetre had been the same—no alteration in the concentration of the ions would occur, and therefore no salt would be precipitated on mixing the solutions, provided no disturbing secondary action occurs.

Solubility product.—It is sometimes convenient to discriminate between the total or apparent solubility of a salt, and the amount of the non-ionized salt present in the solution. The latter is sometimes called the real solubility of the salt. In a saturated solution the real solubility, like the apparent solubility, must be constant. Hence, in the dilution law for sodium chloride $[Na^{\cdot}][Cl'] \rightleftharpoons K\,[NaCl]$, indicated above, the concentration [NaCl] is invariable, K is constant, and consequently also the product of the two is constant. Therefore, we can write for saturated solutions

$$[Na^{\cdot}][Cl'] = \text{Constant}$$

This relation means that in a saturated solution, the product of the "molecular" concentrations of the ions is constant. This product is sometimes called the **solubility product** because, from what has been already stated, the product of the two ion concentrations determine the magnitude of the "real" solubility of the substance.

Familiar examples of this phenomenon are the precipitation of sodium or potassium chlorides from saturated solutions by passing hydrogen chloride through the solutions, or by adding a concentrated aqueous solution of the acid. The phenomenon is quite general. Barium chloride may be substituted for sodium chloride, again, nitric acid will precipitate barium nitrate from concentrated aqueous solutions, a nearly saturated solution of silver bromate will give a precipitate of silver bromate, if either silver nitrate or sodium bromate be added to the solution, sodium chlorate added to a saturated solution of potassium chlorate will lead to the precipitation of the last named salt. There are a number of complications in special cases, thus when a nearly saturated solution of sodium chloride is treated with alcohol, or with hydrogen chloride, the solvent combines with the added material, and less is available for the solution of the salt in question, the solute may form polymerized molecules in the solution, etc.

Solubility of mixtures with no common ion.—If potassium nitrate be added to a saturated solution of silver bromate, a number of molecules

of silver nitrate and potassium bromate will be formed by double decomposition, and the solution will be in equilibrium when these four salts have attained a definite concentration, and each salt is itself ionized and is in equilibrium with the corresponding ions The condition of equilibrium is therefore quite complex It may be symbolized

$$\begin{array}{ccccccc} KNO_3 & + & AgBrO_3 & \rightleftharpoons & KBrO_3 & + & AgNO_3 \\ \updownarrows & & \updownarrows & & \updownarrows & & \updownarrows \\ K^{\cdot}+NO_3' & & Ag^{\cdot}+BrO_3' & & K^{\cdot}+BrO_3' & & Ag^{\cdot}+NO_3' \end{array}$$

The net result is that the number of ionized and non-ionized molecules of silver bromate in the solution is lessened, and the equilibrium

$$AgBrO_{3\ \mathrm{solid}} \rightleftharpoons AgBrO_{3\ \mathrm{solution}}$$

is disturbed The original relation is restored by the passage of more silver bromate into solution Similarly, when nitric acid is added to a saturated solution of silver acetate, some silver nitrate is formed, and the equilibrium

$$\text{Silver acetate}_{\mathrm{solid}} \rightleftharpoons \text{Silver acetate}_{\mathrm{solution}}$$

can only regain its former value by the passage of more silver acetate into solution Consequently, the solubility of a salt is often increased in the presence of a compound containing no common ion As before, complications arise owing to the dehydration of the solution by the added substance, etc The dehydrating action is illustrated in the familiar method of preparing hydrogen chloride by dropping concentrated sulphuric acid into a concentrated hydrochloric acid The sulphuric acid abstracts water, and thus diminishes the effective solvent, the hydrogen chloride is then evolved as a gas The action is in part attributed to the repression of the ions of hydrogen chloride at the same time, and the consequent elimination of molecules from the water already saturated with molecules of the same kind The behaviour of many salts is thus not properly described by the "solubility product" law

Rule for precipitation—The solubility product of sodium chloride in solution is not very great, and, in consequence, if concentrated hydrochloric acid be added to a concentrated solution of sodium hydrogen sulphate, $NaHSO_4$, the solubility product of sodium chloride may be exceeded, and that salt will be precipitated The condition of equilibrium of the mixed solutions is

$$\begin{array}{rcl} NaHSO_4 \rightleftharpoons & \left\{\begin{array}{c} Na^{\cdot} \\ + \\ Cl' \end{array}\right. + & \underbrace{\left\{\begin{array}{c} H^{\cdot} + SO_4'' \\ + \\ H^{\cdot} \end{array}\right.} \\ HCl \rightleftharpoons & & \\ & \updownarrows & \updownarrows \\ & NaCl & H_2SO_4 \end{array}$$

Hence, if the product of the "molecular" concentration of any pair of ions (with equal and opposite electrical charges) in a solution be greater than the solubility product for the saturated

solution formed by the union of these ions, that substance will be precipitated, and conversely, if a substance be present in excess, it will be dissolved if the product of the "molecular" concentration of any pair of ions (with equal and opposite electrical charges) in a solution be *less* than the solubility product for the saturated solution formed by the union of these ions

§ 11 Acids and Bases according to the Ionic Hypothesis

Acids —It will be remembered that Gerhardt defined acids to be "salts of hydrogen," the ionic hypothesis expresses a similar idea another way "all acids, when dissolved in water, furnish hydrogen ions" Although many substances not usually called acids when completely ionized furnish hydrogen ions—*e g* potassium hydrogen sulphate, $KHSO_4$, etc —yet their acidic properties are due to the presence of H ions, and consequently it has been said that "there is only one acid, and that is the H ion" The general and characteristic properties of acids are assumed to be the general and characteristic properties of H ions, and thus the H ions are said to have a sour taste, redden blue litmus, conduct electricity in solutions containing them, behave as univalent radicles, etc The basicity of an acid is fixed by the number of H ions furnished by the complete ionization of one molecule of the acid Thus monobasic hydrochloric acid, HCl, furnishes one H ion $HCl \rightleftharpoons H + Cl'$, and dibasic sulphuric acid furnishes two H ions $H_2SO_4 \rightleftharpoons 2H + SO_4''$ Sulphuric acid also furnishes the ions H and HSO_4' so that it behaves also as a monobasic acid when it forms the so called "acid sulphates"

The action of a metal, say zinc, on an acid is usually represented by the equation $Zn + 2HCl = ZnCl_2 + H_2$, the ionic hypothesis assumes that $Zn + 2H + 2Cl' \rightleftharpoons Zn + 2Cl' + H_2$ Since the Cl' ions are but little affected by the change, the last equation reduces to $Zn + 2H = Zn + H_2$ The action is thus independent of the negative ion, for it involves little more than a transfer of the positive electric charges from the two hydrogen ions to the zinc When the solution of zinc chloride is concentrated by evaporation, the Zn and $2Cl'$ ions recombine to form zinc chloride

Bases —Just as an acid has been defined to be a substance which can furnish hydrogen ions when dissolved in water, so bases, according to the ionic hypothesis, are substances which yield HO' ions when dissolved in water The basic properties of bases are due to the OH ions, and in this sense it has been said that "there is only one base, and that is the OH ion" The general and characteristic properties of the bases are supposed to be the general and characteristic properties of the OH' ions Thus the OH' ions are said to have a soapy feel, turn red litmus blue, conduct electricity in a solution containing them, etc The acidity of a base is fixed by the number of OH' ions it furnishes on complete ionization of a molecule of the base Thus, the uniacid bases, like sodium hydroxide, ionize $NaOH \rightleftharpoons Na + OH'$, and the biacid bases, like barium hydroxide, ionize $Ba(OH)_2 \rightleftharpoons Ba + 2OH'$

Many substances contain hydrogen, and they are not regarded as salts of hydrogen Methane, CH_4, ammonia, NH_3, alcohol, C_2H_5OH, etc Again, H_3PO_2 only gives one hydrogen ion per molecule, and the remaining

two hydrogen atoms are not ionizable, for they form an essential part of the cation H_2PO_2' Silicic acid is very slightly soluble in water, so that its aqueous solution has no effect on blue litmus Silicic acid is acid because it forms a salt, sodium silicate Na_2SiO_3, which dissolves in water and ionizes $Na_2SiO_3 \rightleftharpoons 2Na^{\cdot} + SiO_3''$, when electrolyzed

The chemical activity of different solutions containing equivalent amounts of different acids has been referred to the concentration of the H ions in the solution The concentration of the $H^{\cdot}$ ions depends upon the degree of ionization of the different acids Hence the relative strengths of the acids can presumably be expressed in terms of the electrical conductivity of equivalent solutions The speed of a reaction dependent upon an acid is thus connected with the concentration of the H ions Reverting to the measurements given on p 97 for hydrochloric, sulphuric, and acetic acids, although the solutions contained equivalent quantities of replaceable hydrogen per litre, acetic acid has but one two hundredth the activity of hydrochloric acid

	Hydrochloric acid	Sulphuric acid	Acetic acid
Fraction ionized	0 78	0 51	0 004
Relative strength	100	70	0 5

In hydrochloric acid, a greater number of hydrogen ions are ready to react with the metal than with acetic acid, and consequently the available hydrogen in hydrochloric acid is more rapidly exhausted than with acetic acid where but few ions are in a condition to react with the metal at any moment, and consequently the reaction progresses slowly for a long time, as fast as the available ions are exhausted, new ions are formed by the ionization of the molecule of acetic acid (The total number of hydrogen ions is the same in both cases, but the number in a condition to react with the metal at any moment is very different in all three cases)

Similarly, the strength of a solution containing equivalent quantities of the different bases is referred to the concentration of the OH' ions in the solution The strength of a base depends upon the degree of ionization, or on the concentration of the OH' ions The strength of a base can thus be determined from the electrical conductivity In equivalent solutions, bases, like acids, differ very much in strength The alkalies and alkaline hydroxides are very strong bases, for they are ionized to very nearly the same extent as hydrochloric acid in aqueous solution Ammonia is a comparatively feeble base The following numbers represent the relative strengths of a few bases in $\frac{1}{40}$ normal solution on the assumption that the strength of the base is proportional to the electrical conductivity

	LiOH	NaOH	KOH	NH_4OH
Relative strength	100	98	98	2

When a highly dissociated acid is mixed with a salt, the two react, forming another acid and salt The change is reversible, and the reacting system is then a further illustration of the principle of opposing reactions For instance, the action of dilute nitric acid on potassium hypochlorite (p 284), $HNO_3 + KOCl \rightleftharpoons KNO_3 + HOCl$ If both products are highly ionized, there will be no perceptible change in the system, but in the illustration just cited, hypochlorous acid is but feebly ionized, and *since the* H ions of the nitric acid, and the OCl' ions of the potassium hypochlorite react to form feebly ionized hypochlorous acid, the result of the reaction

in dilute solutions is ionized potassium nitrate, and feebly ionized hypochlorous acid

$$\underbrace{H + NO_3'} + \underbrace{K + OCl'} \rightleftharpoons \underbrace{K + NO'_3} + HOCl$$

Similar remarks apply *mutatis mutandis* to the action of a salt on a base, and this explains how feebly ionized ammonium hydroxide is formed in relatively large quantities when highly ionized solutions of potassium hydroxide and ammonium nitrate are mixed together The reaction proceeds almost to the end

$$\underbrace{NH_4 + NO_3'} + \underbrace{K + OH'} \rightleftharpoons \underbrace{K + NO_3'} + NH_4OH$$

When the base is insoluble, it will be precipitated and the reaction will proceed to an end quite apart from the degree of ionization of the reacting compounds This is the case, for example, with ferric, aluminium, zinc, and other hydroxides

$$\underbrace{Fe + 3Cl} + \underbrace{3Na + 3OH'} \rightleftharpoons \underbrace{3Na + 3Cl'} + Fe(OH)_3$$

§ 12 The Strengths of Acids and of Bases

> I have no doubt that fixed salts choose one acid rather than another in order that they may coalesce with it in more intimate union —JOHN MAYOW (1674)

The strength of an acid or base refers to the extent to which the acid or base exhibits acidic or basic properties respectively The terms "affinity," "avidity," and "activity" are sometimes employed synonymously with "strength," but there are objections to each of these The term "strength," too, is often used where "concentration" is really meant. "Concentration" refers to the "quantity of matter in unit volume" expressed in, say, grams per litre, or some other convenient form, say, gram molecules per litre

The action of sulphuric acid on sodium chloride (p 229), which results in the formation of hydrochloric acid, seems to prove that sulphuric acid is stronger than hydrochloric acid, again, when hydrochloric acid is added to a solution of silver sulphate, silver chloride is precipitated The hydrochloric acid expels the sulphuric acid from its combination with silver $Ag_2SO_4 + 2HCl = 2AgCl + H_2SO_4$, and it seems as if hydrochloric acid is stronger than sulphuric acid. These two conclusions are contradictory and there must therefore be a fallacy in our reasoning We have wrongly assumed that the two acids were competing for sodium and for silver under similar conditions This is not the case When hydrochloric and sulphuric acids compete for the sodium, the hydrochloric acid, being volatile, escapes from the system as fast as it is formed, while the non volatile sulphuric acid alone remains behind Again, when sulphuric and hydrochloric acids are competing for silver, the hydrochloric acid carries the silver away from the sulphuric acid as an insoluble precipitate of silver chloride Still further, hydrosulphuric acid is notoriously a very feeble acid, and yet it can displace relatively strong acids from combinations with the metals. Thus, it will precipitate lead sulphide from solutions of lead chloride, copper sulphide from solutions of copper sulphate, etc.

Here again, the feeble acid does its work by removing the metal from the solution as an insoluble sulphide

To compare the relative strengths of the acids, and, *mutatis mutandis*, of the bases, it is necessary that the comparison be made under conditions where the reacting acids and the products of the reaction are in the same physical condition—say, all in solution Thus, if an equivalent of a solution of sodium hydroxide be mixed with an equivalent of a solution of sulphuric and of hydrochloric acids, the two acids can compete for the one base under the same conditions, and hence the stronger acid will be able to unite with more sodium than the weaker acid It is found experimentally that the same result is obtained when equivalent quantities of sodium hydroxide, sulphuric acid, and hydrochloric acid are mixed together as when equivalent quantities of sodium sulphate and hydrochloric acid, or equivalent quantities of sodium chloride and sulphuric acid are mixed, provided, of course, the whole of the system has been allowed to stand long enough for equilibrium This fact is represented by the equation

$$2HCl + Na_2SO_4 \rightleftharpoons 2NaCl + H_2SO_4$$

In 1803, C L. Berthollet wrote

> I maintain that whenever several acids act upon one alkaline base, the action of one of the acids does not overpower that of the others so as to form an insulated compound, but each of the acids has a share in the action proportionate to its capacity for saturation and its quantity

The proportions of a base shared between two acids, or of an acid between two bases, cannot be determined by the ordinary methods of chemical analysis without disturbing the equilibrium of the mixture The distribution of an acid between two bases, or of a base between two acids, must be determined by physical processes which do not interfere with the solution In illustration, the heat of neutralization of sodium hydroxide by sulphuric acid is 31 38 Cals, and by hydrochloric acid, 27 48 Cals If, therefore, on mixing hydrochloric acid with sodium sulphate, all the sulphuric acid were displaced by the hydrochloric acid, the thermal effect resulting from the decomposition of the sodium sulphate, and the formation of the sodium chloride would be 27 48 − 31 38 = −3 9 Cals After making a small allowance for secondary reactions between sodium sulphate and sulphuric acid, J Thomsen found that the thermal value of the reaction was −2 6 Cals Hence it follows that −2 6 ÷ −3 9 or about two-thirds of the hydrochloric acid combines with about two thirds of the base to form sodium chloride, and about one third of the sulphuric acid combines with the other third of the base to form sodium sulphate A similar result was obtained with a mixture of sodium chloride and sulphuric acid Consequently, in the competition of sulphuric and hydrochloric acids for sodium under comparable conditions, the hydrochloric acid can hold twice as much of the base as the sulphuric acid, and consequently, hydrochloric acid is nearly twice as strong as sulphuric acid

Similar results have been obtained by measuring the specific gravity, index of refraction, absorption of light, etc The relative strengths of the different acids have also been determined by measuring the effects of the different acids on the speed of hydrolysis of cane sugar, methyl acetate, etc The actual numbers obtained by the different methods are not always quite the same, possibly because of the different conditions under which the experiments are made The results obtained by three different methods are shown in Table XIX.

TABLE XIX.—RELATIVE STRENGTHS OF ACIDS

Acid	Thomsen's thermal process	Ostwald's specific gravity process	Molecular conductivity
Hydrochloric acid	100	98	100·0
Nitric acid	100	100 00	99 6
Hydrobromic acid	89	95 00	100 0
Sulphuric acid	49	66 7	65 1
Phosphoric acid	25	—	7 3
Acetic acid	3	1 23	0 4

§ 13 The Neutralization of Acids and Bases

The term "neutral" has been used somewhat vaguely, implying that the substance is neither acidic nor basic The test for acidity or basicity depended upon the behaviour of the solution towards a solution of litmus. If other indicators are used, the conclusions might be different, because a substance might appear acidic towards one indicator, and neutral towards another The ionic hypothesis, as we have seen, refers acidity to the presence of hydrogen ions, and alkalinity to the presence of OH′ ions, and the term "neutrality" refers to the case where the concentration of both ions are the same, or both ions are absent We have seen that water is a constant product of the reaction between the solution of an acid and of a base $HCl + KOH \rightleftharpoons KCl + H_2O$, $H_2SO_4 + 2NaOH \rightleftharpoons Na_2SO_4 + 2H_2O$, etc These reactions are, no doubt, slightly reversible, and the formation of feebly ionized water leads to the removal of the OH′ and the H· ions from the solution, and the reaction is almost completed

$$\underbrace{H^{\cdot}+Cl'}+\underbrace{K^{\cdot}+OH'} \rightleftharpoons \underbrace{K^{\cdot}+Cl'}+H_2O$$

What is here stated with respect to hydrochloric acid and potassium hydroxide applies *mutatis mutandis* to any strongly ionized acid and base, and consequently, the neutralization of strongly ionized acids and bases involves little more than the formation of water $H^{\cdot} + OH' \rightleftharpoons H_2O$, because the other ions present before the acids and bases are mixed remain after the reaction is over If, however, the water be evaporated from the solution, the ions recombine to form the salt, and the result of the reaction is then correctly symbolized $HCl + KOH \rightleftharpoons KCl + H_2O$ This reaction probably also occurs if very concentrated solutions or solids are mixed, whereas the neutralization of acids and bases in dilute solutions involves the formation of water, not salt molecules

The heat of neutralization—This view is further supported by the fact that with dilute solutions of the strong acids and bases, the thermal value of the process of neutralization—heat of neutralization—is the same For example,

Hydrochloric acid	LiOH 13 7	NaOH 13 7	KOH 13 7	$Ca(OH)_2$ 13 8	$Ba(OH)_2$ 13 8 Cals
Sodium hydroxide	HCl 13 7	HBr 13 8	HI 13 7	HNO_3 13 7	HIO_3 13 5 Cals

Hence the heats of neutralization of dilute solutions of the strong acids and bases do not depend upon the specific nature of the acid or base, the formation of water in these reactions is accompanied by the evolution of approximately 13 7 Cals of heat

The law only describes the thermal effect attending the neutralization of solutions sufficiently diluted to ensure complete ionization of acid, base, and salt, it presupposes that no new electrically neutral molecules are formed. As a corollary, it follows that if two completely ionized salts are mixed, there will be no thermal change provided the salts are completely ionized before and after the mixing, and no other electrically neutral molecules are formed The fact that "if two neutral salt solutions at the same temperature are mixed together, no change of temperature occurs" was discovered by H Hess in 1841, and is called Hess' law of thermo-neutrality The ionic hypothesis indicates clearly the conditions which must be fulfilled before Hess' law of thermo-neutrality is applicable

If the acid and base are but partially ionized, the heat of neutralization is not only determined by the heat of formation of water—13 7 Cals —but it is also determined by the thermal value of the energy required to complete the ionization of acid and base When a dilute solution of hydrofluoric acid is neutralized by sodium hydroxide, for example, the sodium fluoride formed during the reaction is fully ionized, whereas the hydrofluoric acid at the commencement of the process $HF + NaOH = NaF + H_2O + 16$ 27 Cals is not fully ionized Hence in addition to the formation of water, there is a continuous ionization of hydrofluoric acid *during* the process of neutralization, and the fact that more heat is produced has been assumed to prove that the ionization of the acid is accompanied by the evolution of heat The heat of neutralization of hypochlorous acid, HOCl, by sodium hydroxide, NaOH is $HOCl + NaOH = NaOCl + H_2O + 9$ 8 Cals., a number less than the normal value 13 7 Cals The salt, NaOCl and the base, NaOH, are completely ionized, while the acid, HOCl, is but feebly ionized Hence, it is assumed that the ionization of HOCl is an endothermal process Similarly, when ammonia is neutralized: $NH_4OH + HCl = NH_4Cl + H_2O + 12$ 2 Cals, it is assumed that the low results are due to the absorption of heat during the ionization of ammonium hydroxide

Hydrolysis —It will be remembered (p 143) that in hydrolysis, a salt reacts with water to form the free base and free acid, or free acid and a basic salt Hydrolysis is thus a reversion of the process of neutralization Hydrocyanic acid, HCy, for instance, ionizes: $HCy \rightleftharpoons H^{\cdot} + Cy'$ With potassium cyanide, KCy, in aqueous solution, $KCy \rightleftharpoons K^{\cdot} + Cy'$ In the latter case, some of the $H^{\cdot}$ ions of the water unite with the Cy' ions of the salt to form molecules of hydrocyanic acid, HCy The equilibrium is disturbed, and more molecules of water ionize: $H_2O \rightleftharpoons H^{\cdot} + OH'$. The new $H^{\cdot}$ ions combine with more Cy' ions and the process continues until the concentration of the OH' ions becomes large enough to prevent the further ionization of the water The solution then contains an excess of OH' ions, and free hydrocyanic acid, as well as potassium cyanide, and the ions $K^{\cdot}$ and Cy' The free hydrocyanic acid can be recognized by its smell, and the OH' ions can be recognized by the alkalinity of the solution

The ionic hypothesis in analytical chemistry—The language of the ionic hypothesis has penetrated into analytical chemistry—particularly qualitative analysis—so that the standard tests for the metals and the acid radicles are described as tests for the respective ions Many, however, doubt if anything will be gained by describing the facts of an eminently practical art in the language of a hypothetical doctrine Be that as it may, since both the chlorides and hydrochloric acid are supposed to furnish Cl'-ions on ionization, it is assumed that the test for hydrochloric acid or a chloride is a test for chloride ions The silver nitrate used in making the test is also supposed to be ionized. Consequently, when a solution of silver nitrate is added to a solution of sodium chloride, the solution is supposed to momentarily contain $Ag^{\cdot} + NO_3' + Na^{\cdot} + Cl'$ ions, but since silver chloride is but slightly soluble in water, the little which is formed by contact of silver and chlorine ions precipitates at once Again, silver chlorate is soluble in water, and accordingly, when silver nitrate is added to a solution of potassium chlorate there is no precipitation and the solution contains four kinds of ions $Ag^{\cdot} + NO_3' + K^{\cdot} + ClO_3'$ Hence, silver nitrate is a test for chlorine but not for chlorate ions

If potassium cyanide, KCy, in aqueous solution be added to a solution of silver nitrate, $AgNO_3$, a precipitate of silver cyanide is formed $Ag^{\cdot} + NO_3' + K^{\cdot} + Cy' = AgCy + K^{\cdot} + NO_3'$ If an excess of potassium cyanide be added, the precipitate redissolves, and it can now be shown that the solution no longer contains the equivalent of $Ag^{\cdot}$ ions in appreciable quantities, since (1) sodium chloride gives no precipitation of silver chloride, (2) on electrolysis, silver is deposited on the anode, not the cathode, as when a solution of silver nitrate is electrolyzed, and (3) a crystalline compound $KAgCy_2$ is obtained when the solution is concentrated. It is assumed, therefore, that the solution of silver cyanide in potassium cyanide ionizes thus $KAgCy_2 \rightleftharpoons K^{\cdot} + AgCy_2'$

Questions

1 What is Ostwald's dilution formula for weak electrolytes? Deduce it theoretically Explain clearly how the constant is experimentally obtained —*St Andrews Univ*

2 What is meant by "electrolysis"? Illustrate your answer by reference to the electrolysis of aqueous solutions of metallic salts —*St Andrews Univ*

3 Write the following equations according to the ionic hypothesis (*a*) Calcium hydroxide and hydrochloric acid, (*b*) Barium chloride, and sulphuric acid —*Univ of Pennsylvania, U S A*

4 Explain in terms of the electrolytic dissociation theory (*a*) The interaction of a solution of copper sulphate with metallic iron (*b*) The electrolysis of copper chloride, (*c*) The interaction of a solution of silver nitrate and hydrochloric acid, (*d*) Neutralization, (*e*) The behaviour of hydrogen chloride in toluene solution and in water solution —*Princeton Univ, U S A*

5 In terms of the ionic theory, what is a strong acid?—a strong base?—a weak acid?—a weak base?

In these terms classify the following —HCl, NH_4OH, KOH, H_2S, H_2CO_3, $Al(OH)_3$ —*Amherst Coll, U S A*

6 Define "acids," "bases," and "salts" in terms of (*a*) their properties, (*b*) their composition, and (*c*) the ionic theory

7 Give a brief history of the word "acid" with an account of its application in the present day What do you understand by the term "ortho acid"?—*London Univ*

8 Give an account of the ionic theory of solution, stating clearly the experimental facts on which it is based —*Aberystwyth Univ*

CHAPTER XVII

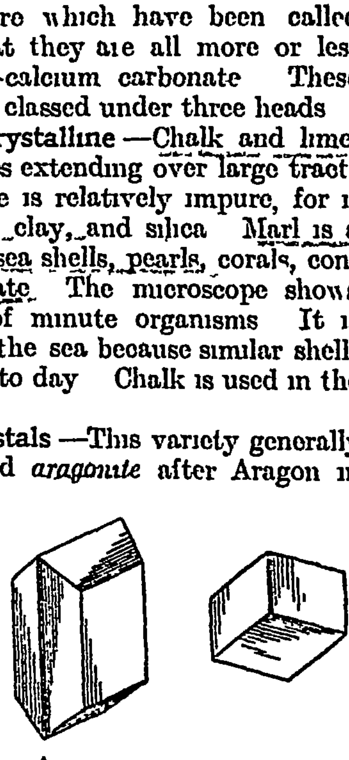
The Alkaline Earths

§ 1 Calcium Carbonate.

Several different minerals occur in nature which have been called different names, although analysis shows that they are all more or less impure forms of one chemical substance—calcium carbonate These different forms of calcium carbonate may be classed under three heads

1 **Calcium carbonate not markedly crystalline**—Chalk and limestone usually occur in large masses sometimes extending over large tracts of country This form of calcium carbonate is relatively impure, for it contains more or less magnesium carbonate, clay, and silica Marl is a mixture of limestone and clay Egg shells, sea shells, pearls, corals, contain a large percentage of calcium carbonate The microscope shows that *chalk* consists largely of the shells of minute organisms It is inferred that these organisms once lived in the sea because similar shells are dredged from the bottoms of the oceans to day Chalk is used in the manufacture of whiting

2 **Calcium carbonate in rhombic crystals**—This variety generally occurs in needle like crystals, and is named *aragonite* after Aragon in Spain If calcium carbonate be prepared in solutions at temperatures exceeding 30°, crystals corresponding with aragonite are formed, and if at temperatures below 30°, crystals of calcite are formed. The fundamental form of crystals of aragonite is illustrated by the outline drawings, Fig 130 Aragonite has a specific gravity about 2 9, calcite 2 72, the former is less rapidly attacked by acids than the latter



Aragonite Calcite

Fig 130 —Dimorphous Crystals of Calcium Carbonate

3 **Calcium carbonate in trigonal crystals**—This form of calcium carbonate occurs in more or less well-defined crystals modelled after a rhombohedron, Fig 130, but exhibiting a great variety of derived shapes which have received special names—"dog's tooth spar," "nail-headed spar," etc When transparent and colourless, trigonal calcium carbonate is called *Iceland spar*, and if opaque and clouded, *calcite* or calcspar A compact fibrous variety with a satin-like lustre is called "satin spar" *Marble* is made up of minute crystals of calcite *Onyx* is a variety which is streaked and coloured by associated impurities.

§ 2 The Action of Heat on Calcium Carbonate

If any one of these forms of calcium carbonate be heated by means of a gas blow pipe flame in a hard glass or quartz test tube, fitted with a gas delivery tube as illustrated in Fig 44, a gas called carbon dioxide, symbolized CO_2, collects in the gas jar, and a residue called calcium oxide or quicklime, symbolized CaO, remains in the test tube The gas will be studied later It is sufficient to state here that the moist gas reddens blue litmus, and unites with bases to form salts called carbonates. If, say, 1 00 gram of pure calcium carbonate be thoroughly calcined in a crucible, 0 56 gram of calcium oxide is obtained, and 0 44 gram of carbon dioxide is expelled as gas If a current of carbon dioxide be passed over calcium oxide, calcium carbonate, symbolized $CaCO_3$, is formed $CaO + CO_2 = CaCO_3$. A certain amount of heat is developed during this latter reaction. Calcium carbonate is undoubtedly a chemical compound of calcium oxide and carbon dioxide

If calcium carbonate be heated in a closed vessel, at different temperatures, when the system is in equilibrium the state of the system will be represented by a point on the curve, Fig 131, where the pressures in the closed vessel are plotted at different temperatures. There are three phases —CaO, $CaCO_3$, and CO_2, and two components—CaO, and CO_2 The system is therefore univariant, meaning that the concentration—that is the pressure—of the gas has one fixed definite value for each temperature This constant pressure is called the dissociation pressure. The dissociation pressure of calcium carbonate is analogous, in many ways, with the vapour pressure of a liquid in a closed space Gaseous molecules of carbon dioxide are continually leaving the dissociating carbonate, and carbon dioxide is continually recombining with calcium oxide When the speeds of the two reactions are the same, the system is in equilibrium The carbonate can only dissociate completely into calcium oxide and carbon dioxide if the latter be continuously removed from the reacting system If the pressure, at any temperature, exceeds the limit indicated by the curve, calcium carbonate will be formed until the pressure of the gas attains the fixed value, constant for the given temperature, and conversely, if the pressure be less than that described by the curve, calcium carbonate will dissociate until the required pressure is attained. If the pressure of the gas be great enough, the calcium carbonate may be fused with no appreciable dissociation On solidification, the mass has a crystalline structure like marble

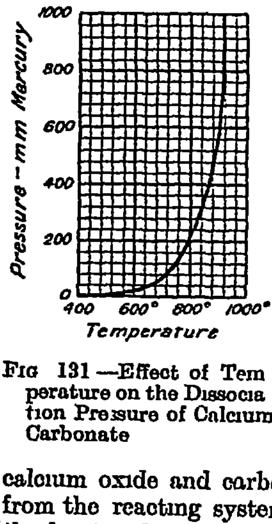


FIG 131 —Effect of Temperature on the Dissociation Pressure of Calcium Carbonate

It is assumed that all solids, calcium carbonate and calcium oxide, exert a small vapour pressure which is generally too small to come within the range of the instruments at present available for such measurements This vapour pressure is further assumed to be constant at any given temperature, like the vapour pressures of substances which are accessible to measurement, and is also unaffected by the quantity of solid present.

According to the law indicated in connection with the iron-steam reaction, the velocity of the dissociation of calcium carbonate will be proportional to the concentration of the carbonate, and equal to the product of the concentration C of the carbonate and the affinity constant k, the velocity of formation of the calcium carbonate will similarly be equal to the product of the concentration of the calcium oxide, C_1, and of the carbon dioxide, C_2, with the affinity constant k' of that reaction Consequently, if these two velocities are the same, the system will be in equilibrium, and $kC = k'C_1C_2$ The concentration, that is, the number of molecules of carbon dioxide per litre, is proportional to the partial pressure p of that gas The concentrations C and C_1 are constant, p 99 and consequently, at any given temperature, $p =$ constant This means that the dissociation pressure of the carbon dioxide is constant, and independent of the extent to which the calcium carbonate has dissociated, provided all the carbonate has not dissociated This same conclusion was obtained in applying the phase rule The principles here stated also apply to the dissociation of mercuric oxide, of hydrates, and of barium peroxide, as previously indicated.

§ 3 Calcium Oxide and Calcium Hydroxide

Calcium oxide is nearly always made by calcining the carbonate—marble, Iceland spar, limestone The residue is variously styled "quicklime," "live lime," "burnt lime," or "caustic lime"—from the Greek καυστικός (kaustikus), burnt (Calcium oxide, when pure, is a white amorphous powder If heated intensely, say in the oxyhydrogen blowpipe, it becomes incandescent, p 101 In the electric furnace, calcium oxide can be melted at a temperature about 2570°, and at a still higher temperature, it can be boiled When a few drops of water are allowed to fall on a (cold) lump of freshly "burned" calcium oxide, which has not been burned at too high a temperature, a hissing noise is produced, and clouds of steam arise Much heat is developed, and the lump of calcium oxide disintegrates into a fine powder called "slaked lime," or calcium hydroxide The term "lime" is often applied to quicklime calcium oxide, and also to slaked lime, calcium hydroxide Moist lime turns red litmus blue If one gram of calcium oxide be treated with water in a weighed dish, and the result of the reaction be thoroughly dried by heating to 150°, 5 6 grams of calcium oxide furnish 7 4 grams of calcium hydroxide, showing that 56 grams of calcium oxide unites with 18 grams of water to form calcium hydroxide—$CaO\ H_2O$, or as is more commonly symbolized, $Ca(OH)_2$, and the reaction is written $CaO + H_2O = Ca(OH)_2$ When calcined at 100°, calcium hydroxide loses no water, at 400°, 30 per cent of the possible water is expelled, and at 450°, nearly all the water may be driven off When a considerable amount of calcium hydroxide is suspended in water, the mixture is called "milk of lime," and if the mixture be allowed to stand, a clear liquid collects above the white sediment The solution—called "lime water"—has a characteristic taste, and it turns red litmus blue At ordinary temperatures, 10°, 100 c c of water dissolves 0 17 gram of the hydroxide, $Ca(OH)_2$ The solubility diminishes with rise of temperature, for instance, the solubility decreases from 0 185 gram of $Ca(OH)_2$ at 0°, to 0 128 at 50°, and 0 077 at 100° per 100 grams of water

When lime water is exposed to the air it soon becomes covered with a film of calcium carbonate owing to the absorption of carbon dioxide from the atmosphere $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$

Mortar is a thick paste made by mixing slaked lime with sand and water Mortar sets or hardens on exposure to the air owing to the loss of water, and the absorption of carbon dioxide from the atmosphere It appears as if a colloidal calcium hydroxide is formed when lime is wetted, and this on drying "sets" by a process analogous with the drying of glue The formation of calcium carbonate is quite a late stage in the setting In the mortars of some of the buildings of the ancient Romans, crusts of minute calcium carbonate crystals protect the inner cores of calcium hydroxide An exposure of 2000 years has not been sufficient to convert more than thin superficial layers of the colloidal hydroxide into carbonate A little of the colloidal hydroxide seems to pass into the crystalline condition The sand makes the mass more porous, and facilitates the rapid absorption of carbon dioxide, and it prevents undue shrinkage during setting The sand is scarcely altered during the action If mortar be placed between bricks or stones, part of the water is absorbed by the bricks and part is lost by evaporation, and the mortar, when set, holds the bricks or stones firmly in place If mortar is to be used for plastering walls, it is mixed with hair which makes the wet mortar stick better

Uses of lime —Lime is used in preparing mortars and cements, as a flux in metallurgy, in the manufacture of glass, bleaching powder, calcium carbide, in purifying illuminating gas, in removing hair from hides before tanning, in drying gases as a disinfectant in marling soil, as a neutralizing agent for acids in chemical industries, etc

Manufacture of quicklime —Limestone is frequently "burned" in a cavity cut in a hill-side, or in a kiln made from bricks or blocks of lime stone The kiln is loosely filled with limestone, or alternate layers of limestone and fuel A fire is built at the base of the stack, and when the burning is complete, the fire is allowed to die out, and the lime is removed In the more recent "shaft kilns," producer gas is led into the shaft near the base, and the hot products of combustion pass up the stack and decompose the limestone The kiln is charged at the top, and the burned lime is raked out through openings at the bottom of the stack The process is continuous—lime is charged in at the top as fast as it is removed at the bottom

Hydraulic cements —Calcareous marls or mixtures of limestone, clay, and sand in the right proportions are heated until the mixture begins to sinter The "clinker" so obtained is ground to powder, and the product called "cement," because if it be mixed with water it sets to a hard stone-like mass, even if exposed to the continued action of water The cement is consequently used for work under water—bridge-piers, etc —under conditions where mortar would disintegrate and soften Several varieties are on the market under various names—Portland cement, hydraulic cement, etc The ground clinker appears to consist mainly of a solid solution of lime, silica, and alumina which, for convenience, is sometimes called alite The setting of the wetted cement appears to be the joint effect of several different actions not yet clearly understood The main reaction is probably due to the formation of colloidal calcium alumino silicates when "alite" is wetted These decompose, forming crystals of

tricalcium aluminate and a number of different substances in a colloidal condition The gradual desiccation of the colloids leads to the gradual hardening of the mass, the desiccation appears to proceed even when the cement is immersed in water

§ 4 Strontium and Barium Oxides and Hydroxides.

Strontium carbonate is found in nature in the mineral *strontianite*, $SrCO_3$, and barium carbonate in the mineral *witherite*, $BaCO_3$ Barium carbonate decomposes at about 1842°, strontium carbonate at 1150°, and calcium carbonate at 825°. When strontium carbonate is calcined, strontia, that is, strontium oxide, SrO, is formed, witherite furnishes baryta, *i e* barium oxide, BaO Strontia is made on a large scale by heating the carbonate in superheated steam, carbon dioxide is evolved, and strontium hydroxide, $Sr(OH)_2$, is formed $SrCO_3 + H_2O = Sr(OH)_2 + CO_2$ The strontium hydroxide on ignition furnishes strontium oxide $Sr(OH)_2 = SrO + H_2O$. Barium carbonate requires so high a temperature for its decomposition that the raw material is mixed with lampblack or tar before calcination. The carbon burns off, and the carbonate, at the same time, is decomposed at a much lower temperature $BaCO_3 + C = BaO + 2CO$

Like calcium oxide, both strontia and baryta slake in contact with water with the evolution of much heat In the case of baryta, the heat is so great that if but little water be used, the mass may become visibly red hot The heats of formation of the different hydroxides are $Ca(OH)_2$, 16 25 Cals, $Sr(OH)_2$, 17 70 Cals, and $Ba(OH)_2$, 22 26 Cals Barium hydroxide is usually made by heating a mixture of *barytes*—barium sulphate, $BaSO_4$—with powdered coke, or coal Crude barium sulphide is formed $BaSO_4 + 4C = 4CO + BaS$ The latter is then heated in a stream of carbon dioxide, and thus converted into barium carbonate $BaS + CO_2 + H_2O = BaCO_3 + H_2S$ Barium carbonate is converted into the hydroxide by heating it in superheated steam as just indicated for strontium carbonate Strontium hydroxide is formed in a similar manner from the mineral *celestine*—strontium sulphate, $SrSO_4$ Strontium hydroxide is used in the manufacture of sugar Strontium hydroxide is more soluble in water than calcium hydroxide, and barium hydroxide is more soluble than strontium hydroxide The solubilities of the three hydroxides in grams per 100 c c of water are

	0°	50°	100°
Calcium hydroxide	0 18	0 13	0 08
Strontium hydroxide	0 41	2 5	21 7
Barium hydroxide	1 67	13 12	101 4

Unlike calcium hydroxide, barium hydroxide can be fused without decomposition Aqueous solutions of both barium and strontium hydroxides deposit crystals with eight molecules of water—*e g* $Ba(OH)_2 8H_2O$ Like strontium hydroxide, barium hydroxide is dehydrated when heated high enough, forming barium oxide If calcined in air, barium oxide, BaO, forms barium peroxide BaO_2, as previously indicated Barium, calcium, and strontium peroxides are made by adding hydrogen peroxide to solutions of the corresponding hydroxides The peroxides crystallize out with eight molecules of water—*e g* $CaO_2 8H_2O$ The hydrated peroxides lose water at about 130°, forming the corresponding anhydrous peroxides When more strongly heated they decompose, giving oxygen $2CaO_2 = 2CaO + O_2$.

§ 5 Metallic Calcium, Strontium, and Barium.

Impure calcium was made by H Davy in 1808, and the pure metal was made by H. Moissan, in 1898, by reducing calcium iodide with sodium. The metal is now made by electrolysis of the fused chloride, $CaCl_2$ In G O Seward and F von Kügelgen's process (1908), the anode is a graphite crucible, and the cathode a rod of iron which dips in the fused chloride When the current passes, metallic calcium collects at the lower end of the cathode Calcium chloride fuses at a lower temperature than metallic calcium, and the temperature is so regulated that the calcium solidifies on the cathode An irregular rod of metallic calcium is made by slowly raising the cathode The end of the calcium rod, dipping in the fused chloride, then forms the lower end of the cathode The rod of metallic calcium dipping in the bath is also cooled by an annular tube through which cold water flows Metallic strontium and barium, more or less impure, were first prepared by a similar process to that used for metallic calcium by H. Davy about 1808

Properties—Calcium is a silver white lustrous metal It tarnishes slowly in air, and when heated in an atmosphere of hydrogen, it forms calcium hydride, CaH_2, and in an atmosphere of nitrogen, calcium nitride, Ca_3N_2, in air, calcium oxide, CaO, and with chlorine, calcium chloride, $CaCl_2$ The interaction of water and calcium is rapid, but not violent Hydrogen and calcium hydroxide are produced: $Ca + 2H_2O = Ca(OH)_2 + H_2$ A crust of calcium hydroxide, $Ca(OH)_2$, forms on the surface of the metal, and slows down the reaction If an acid be present, the reaction is rather violent. The properties of strontium and barium resemble those of metallic calcium

Atomic Weights—Analyses of calcium chloride, calcium carbonate, etc, give numbers corresponding with a combining weight between 40 03 and 40 23, the best representative value is taken to be 40 09 (oxygen = 16) Several different lines of evidence, to be discussed later, show that this number is not far from the atomic weight. According to Dulong and Petit's rule, for example, the quotient of 6 4 divided by the specific heat of a solid element is a close approximation to the atomic weight of that element The specific heat of calcium is 0 152 Hence 6 4 ÷ 0 152 = 42 approximates to the atomic weight of calcium Barium and strontium respectively furnish the numbers 137 37 (extremes 137 10 and 137 38) and 87 63 (extremes 87 37 and 87 68) for the atomic weights

Occurrence of these elements in nature—The free elements do not occur in nature Calcium compounds are rather abundant The occurrence of calcium as carbonate has already been discussed. Calcium also occurs as sulphate in *gypsum or selenite*, $CaSO_4.2H_2O$, as calcium fluoride, CaF_2 in *fluorspar*, as calcium phosphate in *phosphorite*, etc (*q v*) The carbonate and sulphate are common in spring and river water Calcium compounds occur in all animal and vegetable organisms Bones contain a large proportion of combined calcium The chief natural compounds of barium and strontium have already been indicated—*strontianite*, $SrCO_3$, and *celestine*, $SrSO_4$, *heavy spar* or *barytes*, $BaSO_4$, and *witherite*, $BaCO_3$. It is worthy of note that if any two of these elements are found in the same mineral, the pairs will probably be barium and strontium, or strontium and calcium, for barium and calcium do not usually pair together

in the absence of strontium—e g strontium is common in witherite, strontium in aragonite, and calcium in celestine

History —The name "calcium" is derived from the Latin *calx*, for lime Lime was not distinguished from the other earths by the early chemists, but towards the middle of the eighteenth century lime was recognized as a distinct earth

"Strontium" is named after Strontian, a village in Argyllshire (Scotland), where strontianite was first found (1787) The mineral was first confounded with barium carbonate In 1790, A Crawford suggested that strontianite contained a peculiar earth, and based his opinion on the experiments of W Cruickshank. The suggestion was confirmed by T C Hope (1792), and by M H Klaproth (1793)

V Casciorolus, in 1602, noticed that when heavy spar was calcined with combustible matters, the product became phosphorescent in the dark. He called the stone *lapis solis*, and later, it was called "Bolognian," or Bononian phosphorus The heavy spar which furnished *lapis solis* was at first believed to be a peculiar kind of gypsum K W Scheele (1774) found that the mineral contained a new earth which gave a sulphate insoluble in water G de Morveau called the earth "barote"—from the Greek *βαρύς* (barus), heavy—and Lavoisier later altered the word to "baryta," the name now used for this earth

§ 6 The Relations between Calcium, Strontium, and Barium

The elements of the alkaline earths—calcium, barium, and strontium —exhibit a close kinship and display a gradation in their properties from member to member as the atomic weight increases in passing from calcium to barium The elements become more active chemically as their atomic weight increases, the specific gravities of the elements and compounds increase, the basic properties and solubilities of the hydroxides increase, and the solubilities of the halides, nitrates, sulphates, and chromates decrease The physical properties of the elements are indicated in Table XX.

TABLE XX —PHYSICAL PROPERTIES OF THE ALKALINE EARTH METALS

——	Calcium	Strontium	Barium
Atomic weight	40 09	87 63	137 37
Specific gravity	1 52	2 55	3 75
Atomic volume	26 4	35 15	36 6
Melting point	780°	800°	850°
Specific heat	0 152	—	0 068
Flame coloration	Brick-red	Crimson	Green
Heat of formation of monoxide R″O Cals	131 3	130 98	130 38

The metals are fairly stable in air, they quickly tarnish in ordinary air, and when heated, they burn to the monoxide, they are all bivalent, they combine with water with the evolution of hydrogen at ordinary

temperatures, and form soluble oxides of the type $R''O$, hydroxides of the type $R''(OH)_2$, and peroxides of the type $R''O_2$. The salts are discussed under "Chlorides," "Sulphates," "Nitrates," "Sulphides," etc. The normal carbonates are but sparingly soluble in water, the unstable acid carbonates are more soluble. The low solubility of the carbonates, chromates, and sulphates is utilized in analytical work. All three carbonates are precipitated when ammonium carbonate is added to solutions of their salts. Radium, in this family of elements, will be discused later.

Questions

1. What is lime? How is it obtained? What takes place (*a*) when lime is mixed with water, (*b*) when it is heated strongly with sand, (*c*) when it is exposed to carbon dioxide gas? Give equations.—*Aberdeen Univ.*

2. Distinguish between quick lime, slaked lime, lime water, and milk of lime. What do they absorb from the air?—*Sheffield Scientific School, U. S. A.*

3. Give the names and formulæ of the four principal minerals containing calcium. How is metallic calcium prepared? By what reactions would it be possible to prepare from the metal specimens of (*a*) calcium hydroxide, (*b*) calcium carbonate, (*c*) bleaching powder.—*London Univ.*

4. Marignac found that 5 grams of strontium chloride containing six molecules of water of crystallization gave 3.442 grams of strontium sulphate. Calculate the equivalent of strontium. ($H = 1$, $O = 16$, $S = 32$, $Cl = 35.5$).—*London Univ.*

CHAPTER XVIII

Beryllium, Magnesium, Zinc, Cadmium, and Mercury

§ 1 Beryllium and Magnesium

History of beryllium—While analyzing beryl, in 1797, L N Vauquelin found that a precipitate which he thought to be aluminium hydroxide, dissolved like aluminium hydroxide in potassium hydroxide, but unlike aluminium hydroxide, the solution furnished a white precipitate when boiled for some time Unlike aluminium hydroxide, too, the precipitate was soluble in ammonium carbonate, and behaved in many other ways differently from aluminium hydroxide Hence L N Vauquelin announced the discovery of a new earth—"la terre du Béril," in 1798 The editors of the *Annales de Chemie*, in which the discovery was announced, proposed the name "glucine"—from the Greek γλυκυς (glucus), sweet—because many of the salts of Vauquelin's "le terre du Béril" had a sweet taste Since other salts possessed the same property, the term *beryllia*—derived from the name of the mineral—has almost displaced the term "glucina" from recent chemical literature F Wohler isolated the metal beryllium in 1828 by the action of potassium on beryllium chloride.

Occurrence and extraction of beryllium—The mineral *beryl*, $3BeO.Al_2O_3.6SiO_2$, is the principal source of beryllium The beryls include the gem-stones *emerald* (pale green), and *aqua marine* (pale blue) Beryllium salts can be obtained from beryl by fusing the mineral with sodium carbonate, digesting the resulting mass with hydrochloric acid, evaporating the solution to dryness to separate the silica in an insoluble condition, extracting the soluble matters with dilute hydrochloric acid, precipitating a mixture of aluminium and beryllium hydroxides with ammonia, dissolving the precipitate in potassium hydroxide, and boiling the solution so as to precipitate the beryllium hydroxide The precipitate is re-dissolved in acid and re-precipitated from the potash solution a number of times to ensure its freedom from alumina The hydroxide can then be converted into various salts by dissolving it in the proper acid—hydrochloric acid for beryllium chloride, etc

History of Magnesium—In 1695, N Grew published a pamphlet describing a peculiar salt found in the mineral springs at Epsom The medicinal properties of this salt attracted some attention, in England the salt was called "Epsom-salt," and on the Continent, "sal anglicum" Magnesia alba (a basic magnesium carbonate) came into commerce from Rome about 1700, the term "*magnesia alba*" was applied to the earth owing to some fanciful contrast with "magnesia nigra," the term then used for black oxide of manganese In 1755, J Black clearly distinguished

between magnesia and lime by showing that magnesia furnished a soluble sulphate, and lime a sparingly soluble sulphate When H. Davy isolated the impure metal in 1808, he called it "magnium" At that time, the terms "magnesium" and "manganesium" were applied synonymously to the element (manganese) derived from the mineral pyrolusite (manganese dioxide) To avoid confusion, the term "magnesium" was soon afterwards restricted to the element derived from magnesia alba, and "manganese" to the element derived from pyrolusite [1]

Occurrence of Magnesium—Magnesium occurs in nature combined, not free, as magnesium carbonate in *magnesite*, $MgCO_3$, double carbonate of calcium and magnesium in *dolomite*, $MgCO_3.CaCO_3$, magnesium sulphate in *epsom salts*, $MgSO_4.7H_2O$, and *kieserite*, $MgSO_4.H_2O$, magnesium chloride in *carnallite* and *kainite*, magnesium silicate in *olivine*, Mg_2SiO_4, *enstatite*, $MgSiO_3$, etc Magnesium is also common in many other minerals *e g* asbestos, steatite, spinel, meerschaum, serpentine, talc, etc

Atomic weight—The combining weight of magnesium (oxygen = 16) has been determined by the analysis of the sulphate, oxalate, chloride, etc, and some of the best results lie between 24 26 and 24 39 The best representative value is taken to be 24 32 This agrees with the value for the atomic weight estimated by Dulong and Petit's method of approximation, specific heat, 0 2234, and the isomorphism of some magnesium salts with iron, zinc, manganese, etc, salts Beryllium has an atomic weight approaching 9 1

Preparation of the metals—Magnesium and beryllium are closely related metals, both can be prepared by the electrolysis of the chlorides, or of a mixture of the respective chlorides with potassium chloride In the case of magnesium, fused carnallite can be used The metals can also be made by heating the chlorides with sodium $MgCl_2 + 2Na = 2NaCl + Mg$ Both processes—electrolysis and sodium reduction—are used for magnesium on a large scale Beryllium is of little commercial importance

Properties of magnesium and beryllium—Both metals have a silvery white lustre, and low specific gravity When ignited magnesium burns in air giving a brilliant white light of great actinic power Both metals are slowly oxidized by moist air Magnesium very slowly decomposes boiling water When heated in a current of steam, magnesium takes fire, and continues burning $Mg + 2H_2O = Mg(OH)_2 + H_2$ Magnesium melts at 632°, beryllium a little above 960° Magnesium boils at about 1120° Both metals readily dissolve in dilute hydrochloric and sulphuric acids, magnesium is also rapidly dissolved by nitric acid, and it is perhaps the only metal which gives a copious yield of hydrogen when treated with nitric acid. Beryllium is not readily attacked by nitric acid. Beryllium is dissolved by alkaline hydroxides $Be + 2KOH = Be(OK)_2 + H_2$ The hydroxide thus behaves towards bases like a weak acid. Magnesium is not appreciably attacked under the same conditions. Beryllium seems to bear the same relation to alkaline earths that lithium bears to the alkalies. Magnesium reacts with aqueous solutions of ammonium salts

[1] It is not very clear whether the term "magnesia" is a corruption of the word Mangana in the East Indies, or whether "manganese" is a corrupted form of the word Magnesia, a locality in Asia Minor

forming a double salt with the evolution of hydrogen Magnesium when heated with nitrogen forms magnesium nitride, Mg_3N_2 Magnesium is used in flashlight preparations for photography, and also in making fireworks

Magnesium and beryllium oxides —The oxides can be prepared by igniting the metals in air, as well as by calcining the nitrates, carbonates, and sulphates in the presence of water vapour Magnesium oxide is made from magnesium chloride of the Stassfurt deposits by converting the latter into the carbonate and calcining the resulting carbonate The "magnesia usta" of commerce is made by the prolonged calcination of the carbonate at a low temperature

Magnesia is slightly soluble in water to which it gives a slight alkaline reaction 100 c c of water dissolve about 0 001 gram of magnesia The oxide is not completely converted into the hydroxide by the action of water The hydroxide is precipitated from solutions of magnesium salts by the addition of alkali hydroxides Magnesium hydroxide, $Mg(OH)_2$, is soluble in ammonium salts, and hence the precipitation with ammonia is incomplete $Mg(OH)_2 + 2NH_4Cl \rightleftharpoons MgCl_2 + 2NH_4OH$ If enough ammonium salt be present in the solution, magnesium hydroxide will not be precipitated at all, at the same time, a soluble salt—probably $(NH_4)_2MgCl_4$, that is, $MgCl_2$ $2NH_4Cl$—is formed in the solution

Magnesium oxide fuses at about 2000°, and on account of its refractory qualities, it is used for pencils as an alternative to lime, in the so called "lime-light", and also for making refractory bricks ("magnesia" bricks made from calcined magnesite, and "dolomite bricks" from calcined dolomite), crucibles, cupels, furnace linings, etc A paste made with water and magnesia calcined at a low temperature behaves similarly to lime in mortar It gradually re hydrates, absorbs carbon dioxide from the air, and sets in about twelve hours to a hard mass

§ 2. Zinc, Cadmium, and Mercury—Occurrence and Preparation

History of Zinc —Brass, an alloy of zinc and copper, was known to the ancients, and several references to "brass" occur in the sacred writings R Jagnaux says that bracelets made of zinc have been found in the ruins of Cameros which was destroyed about 500 B C Such knowledge of zinc as was possessed by the ancients appears to have been lost for a time B Valentine first used the word "zinken," but he did not refer to it as a metal Paracelsus first stated zinc to be a metal In the sixteenth century, zinc was brought from China and the East Indies under the name "tutanego" In 1721, J F Henkel discovered that zinc could be obtained from calamine, and a works for the manufacture of zinc was erected at Bristol about 1740 by J Champion Champion's process was patented 1739, in this process the ore was distilled in large crucibles arranged with a pipe extending downwards through the bottom of the crucible It is called the English process of "distillation per descensum." The process is obsolete

Occurrence of Zinc —Metallic zinc has been reported in the basaltic rocks of Victoria (Australia), but it usually occurs combined as carbonate, *zinc spar, calamine*, $ZnCO_3$, sulphide, *zinc blende* or *black jack*, ZnS, oxide, *zincite* or *red zinc ore*, ZnO, silicate, *willemite*, $2ZnO$ SiO_2, *franklinite*, $(ZnFe)O$ Fe_2O_3, *zinc spinel* or *gahnite*, ZnO Al_2O_3

History of cadmium.—The term καδμεια (cadmeia) was applied by Dioscorides, and by Pliny, to a zinciferous earth (calamine)—found on the shores of the Black Sea—which when melted with copper furnished brass—aurichalcum. Pliny also applied the term "cadmia" to the tutty (impure zinc oxide) found in the flues of brass founder's furnaces. In 1817, F Stromeyer discovered a yellow oxide free from iron in a sample of zinc carbonate used at the smelting works at Salzgitter This could only be due to the presence of a new metal which he called "cadmium," from *cadmia fornacum*, because the metal was found in the "flowers of zinc," that is, the flue dust of the zinc furnace

Occurrence of cadmium.—This element does not occur free It is commonly found accompanying zinc in calamine, and zinc blende Very few zinc ores contain more than 0.5 per cent of cadmium. The rare mineral *greenockite*, cadmium sulphide, CdS, is of no commercial importance

Preparation of zinc.—Zinc and cadmium usually occur together The ores employed are the carbonate, oxide, and sulphide The process involves two operations (1) *Roasting*.—The object is to convert the sulphide into the oxide by calcination The oxidation of the carbonate presents no difficulty $ZnCO_3 = ZnO + CO_2$ In the case of the sulphide, the sulphur is oxidized by calcination in air $2ZnS + 3O_2 = 2ZnO + 2SO_2$ (2) *Reduction*.—The crushed oxide is mixed with crushed coke and heated to bright redness in fireclay retorts. The oxide is reduced with the formation of carbon monoxide $ZnO + C = Zn + CO$ The metal distils over and collects in fireclay or iron receivers. At first a fine grey powder—"zinc dust"—collects in the receiver This is a mixture of zinc oxide and powdered metal When the receiver is warm, the metal condenses to a liquid which is drawn off at intervals and cast into plates or bars If zinc sulphate had been produced during the roasting of the sulphide $ZnS + 2O_2 = ZnSO_4$, it would be reduced by the carbon back to the sulphide, and thus reduce the yield of metal by the ore The zinc so obtained—called *spelter*—contains carbon, iron, lead, arsenic, and cadmium as impurities. It may be refined by careful distillation The fireclay retorts have different shapes and different types of condensers are used in different smelting works The prevailing styles are the Silesian, Belgian, and Rhenish.

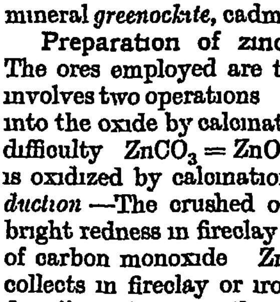


FIG 132.—Belgian Zinc Retort

The so called Belgian retort is an oval or cylindrical tube—6″ to 10″ diameter, and about 3′ or 4′ long The retort is fitted with a conical tube—about 16″ long—as condenser, Fig 132 The wide end fits the retort and the narrow end is fitted with a sheet iron nozzle to catch any zinc dust The retorts are built into the furnace in rows and tiers

Preparation of cadmium.—The first product of the distillation of zinc ores contains most of the cadmium partly as metal, partly as oxide The zinc dust is reduced in clay or iron retorts and redistilled. The product, called "crude cadmium," contains some zinc from which it can be separated by repeated distillation at a low temperature or by electrolysis A solution of cadmium chloride or sulphate—containing up to 30 per cent of cadmium—is electrolyzed with crude cadmium as the anode, and pure cadmium as cathode The cadmium dissolves from the former and is redeposited on the latter There are not enough cadmium ores to

allow cadmium to be extracted for its own sake, and hence the extraction of cadmium is often a "side line" in a zinc smelting works.

History of mercury.—Mercury was mentioned 300 B.C. by Theophrastus as χυτός ἄργυρος (chutos argyros), quicksilver or liquid silver, and he states that it can be made by rubbing vinegar with cinnabar in a copper vessel. Dioscorides called it ὕδωρ ἄργυρος (hydor argyros), liquid silver, hence the Latin *hydrargyrum*, and the present-day symbol Hg. The metal had a certain fascination for the alchemists, and for a time they believed that it, or something similar, was a constituent of all metals. "Nimble volatile mercury" was named after the mythological Mercury, the messenger of the gods, and accordingly the ancient chemists symbolized the metal by the caduceus or herald's wand ☿, also used for the planet Mercury.

Occurrence of mercury.—Free mercury in small quantities occurs disseminated in the ores of mercury. *Cinnabar*, HgS, is the chief ore of mercury, and it is mined in Almaden (Spain), Idria (Carniola), Bavarian Palatinate, Peru, California, Japan, China, etc.

Preparation of mercury.—Mercury is obtained almost exclusively from cinnabar, HgS. The cinnabar is roasted to oxidize the sulphur, and the metal is liberated: $HgS + O_2 = SO_2 + Hg$; or else the ore is distilled with lime in closed retorts whereby calcium sulphide and mercury are formed: $2HgS + 2CaO = 2CaS + 2Hg + O_2$. The former process is generally used, but different condensing arrangements are employed in different works. The mercury, for example, may be condensed in large chambers as at Idria; or in a series of pear-shaped vessels—aludels—connected in rows nearly 50 feet long as at Almaden. About six trains of aludels are connected with one roasting furnace. Crude mercury is sent into commerce in iron bottles holding about 75 lbs. of liquid metal. The mercury may be cleaned by filtration through chamois leather; and purified by distillation from iron retorts. In the laboratory, mercury is often purified by running a fine spray of mercury down a long column of dilute nitric acid (specific gravity 1.1), followed by distillation *in vacuo*.

§ 3 The Properties of Zinc, Cadmium, and Mercury.

Cadmium and zinc are white metals. Zinc is brittle at ordinary temperatures, but ductile at 100°–150°, and it can then be drawn into wire, and rolled into sheets. Cadmium is ductile enough at ordinary temperatures to be rolled into sheets and drawn into wire. Zinc is brittle at 200°, and it can then be readily powdered. Cadmium melts at 320.2°, zinc at 418.2°. Mercury is a silvery-white metal liquid at ordinary temperatures. In thin films, mercury is violet by transmitted light. It solidifies into a malleable solid at −38.85°. Mercury does not tarnish in air. Both cadmium and zinc are slowly oxidized by moist air, and in water containing air in solution, the metals are oxidized with the formation of basic carbonates. Both metals are attacked by dilute hydrochloric and sulphuric acids giving hydrogen; nitric acid gives oxides of nitrogen. Cadmium is insoluble in alkaline hydroxides, but zinc dissolves, giving off hydrogen (*q.v.*). Mercury is not attacked by hydrochloric acid; concentrated sulphuric acid acts very slowly in the cold; but when heated, mercuric sulphate, $HgSO_4$, sulphur dioxide, and some mercurous sulphide are formed. Concentrated nitric acid rapidly attacks mercury, forming

mercuric nitrate and oxides of nitrogen Dilute nitric acid acts slowly giving mercurous nitrate. Alkali hydroxides have no appreciable action on mercury

Amalgams —Mercury is a good solvent for some of the metals The solutions are called "amalgams." The phenomena attending the solution of the metals in mercury appear to be closely analogous with the solution of different substances in water A considerable amount of heat is often developed, as is the case when sodium or potassium metals are dissolved in mercury The freezing points of solutions of potassium in mercury are indicated by the curve, Fig 133 Compare Figs 55 95, etc The breaks in the curve correspond with the formation of the following compounds KHg (melts 178°), KHg_2 (270°), K_3Hg_9 (204°), K_2Hg_9 (173°), KHg_9 (70°) Two well defined eutectics occur at 47° and −43° The numbers in brackets represent melting points. With sodium the following compounds are indicated on the freezing point curve $NaHg_4$ (159°), $NaHg_2$ (360°), NaHg (129°), Na_3Hg_2 (123°), Na_5Hg_2 (62°), Na_3Hg (−34°) When the potassium amalgams are heated to 440° crystalline, KHg_2, remains behind, with sodium Na_3Hg These latter compounds spontaneously inflame when exposed to the air Gold and silver dissolve readily in mercury and this fact is utilized in the extraction of gold (*q v*) Tin amalgam is soft, and is used in making mirrors. Amalgams of gold, copper, and zinc, are used in dentistry for stopping teeth Zinc amalgam is but slowly attacked by sulphuric acid, and amalgamated zinc is used in making batteries. The zinc dissolves only when the circuit is closed

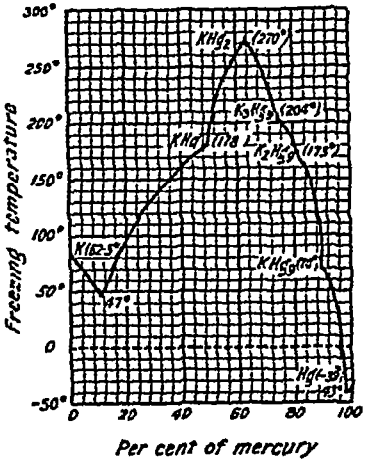


FIG 133 —Freezing Curves of Potassium Mercury Amalgams

The atomic weight of zinc and cadmium —The combining weight of zinc has been determined by the analysis of the halogen compounds, the carbonate, and the sulphate, and the synthesis of the oxide Some of the best results (oxygen = 16) vary between 65 24 and 65 99, and the best representative value is taken to be 65 37, which agrees with the atomic weight estimated from the isomorphism of zinc salts with some salts of magnesium, manganese, etc, the vapour density of volatile compounds of zinc, and Dulong and Petit's method of approximation, specific heat of zinc, 0 0935 The atomic weight of cadmium determined by similar methods is 112 4

The atomic weight of mercury —Some of the best determinations of the combining weight of mercury, by the analysis or synthesis of mercury oxide, sulphide, chloride, bromide, and cyanide give numbers ranging from 199 83 to 200 23 The best representative value (oxygen = 16) is taken to be 200, and this number also corresponds with the atomic weight estimated from the vapour density of volatile compounds of mercury, and the isomorphism of some mercury salts with salts of lead, copper, etc.

Uses.—Zinc is used in making the anode plates of batteries and in making certain utensils. It is also a prevailing constituent in certain alloys: brasses, German silver, bronze, etc. (*q.v.*) Galvanized iron is iron covered with a protective coating of zinc to prevent rusting. In one process of galvanizing, the iron is first cleaned with acid or sand blast, and subsequently dipped in molten zinc; in another process of galvanizing, the zinc is deposited electrolytically, similar to electroplating, described on p. 303. Mercury is used in making certain medicinal preparations—blue pills and mercurial ointments; in making amalgams; and in the manufacture of scientific instruments—thermometers, barometers, etc. Cadmium is used in making certain fusible alloys (*q.v.*)

§ 4. The Oxides of Zinc, Cadmium, and Mercury.

Zinc monoxide, ZnO, and cadmium monoxide, CdO.—The monoxides of zinc and cadmium are formed when the metals are burnt in air: $2Zn + O_2 = 2ZnO$. Zinc oxide, under the commercial name "zinc white," is manufactured by heating zinc in air and passing the fumes into condensing chambers where the oxide collects. Zinc oxide is used in place of white lead as a white pigment where the blackening of white lead is objectionable. (Zinc oxide appears yellow when hot, white when cold.) Cadmium oxide, CdO, has a rich brown colour. Zinc oxide forms hexagonal crystals if heated to a very high temperature; it does not melt even in the oxyhydrogen blowpipe, but, like lime and magnesia, the oxide is vividly incandescent under these conditions, it afterwards appears phosphorescent in the dark.

Zinc hydroxide, $Zn(OH)_2$, cadmium hydroxide, $Cd(OH)_2$.—These hydroxides cannot be produced by the action of water on the oxides, but they are precipitated when an alkaline hydroxide is added to a solution of a zinc or a cadmium salt. Zinc hydroxide, unlike cadmium hydroxide, is soluble in an excess of the alkaline hydroxide, forming salts of the type, $Zn(OK)_2$, called zincates. The same salt is formed when zinc metal is dissolved in potassium hydroxide. Both hydroxides are soluble in ammonia, not because of the acidic character of the hydroxide, but because of the formation of complex ammonio zinc oxide—$3ZnO \cdot 4NH_3 \cdot 12H_2O$. Both oxides are basic and yield salts on treatment with acids.

Zinc and cadmium peroxides.—Both zinc and cadmium form peroxides: ZnO_2 and CdO_2, when the oxides are moistened with hydrogen peroxide. They are probably superoxides, so that they are represented by the constitutional formulæ: $Zn<^{O}_{O}$ and $Cd<^{O}_{O}$. These peroxides are easily decomposed by acids with the evolution of oxygen. The peroxides of zinc and cadmium, and also of magnesium are less stable than the peroxides of the alkaline earths.

Cadmous oxide, Cd_2O.—When cadmium chloride, $CdCl_2$, is heated with metallic cadmium, a lower chloride, cadmous chloride, CdCl, is formed. This when treated with water gives cadmous hydroxide, CdOH, and this, in turn, when gently warmed, gives cadmous oxide, Cd_2O. Zinc does not form an oxide lower than the monoxide, ZnO; hence cadmium, in this respect, is more closely related with mercury, which also forms two oxides, mercuric oxide, HgO, and mercurous oxide, Hg_2O.

Mercurous oxide, Hg_2O.—This oxide is formed as an unstable dark

brown powder when calomel, HgCl, is digested with an alkaline hydroxide $HgCl + KOH = KCl + HgOH$, $2HgOH = Hg_2O + H_2O$, and as a black powder when an alkaline hydroxide is added to soluble mercurous salts No corresponding hydroxide is known Instead of being oxidized in air, mercurous oxide is decomposed when warmed, or when exposed to air in the light, forming mercuric oxide and mercury $2Hg_2O = 2HgO + 2Hg$ Mercurous oxide is feebly basic, and it exhibits no acidic qualities like zinc oxide

Mercuric oxide, HgO —At first sight, this oxide appears to exist in two distinct modifications—red and yellow If a mercuric salt be treated with an excess of alkaline hydroxide in the cold, mercuric hydroxide is probably formed, but this immediately decomposes into yellow mercuric oxide If the precipitation be made from hot solutions, an orange precipitate is obtained. The difference in colour is probably due to the state of subdivision of the precipitate The larger the granules, the redder the tint. If mercuric oxide be prepared by the ignition of the nitrate, or by calcining the metal in air, nearly at its boiling point, the oxide is red and distinctly crystalline, the yellow oxide becomes red when heated to about 400° When heated, the red oxide darkens in colour and finally appears almost black, the red colour returns on cooling If heated above the temperature at which the oxide appears to blacken, it decomposes into mercury and oxygen The yellow oxide is slightly soluble in water, and the solution has an alkaline reaction with basic, but no acidic, qualities

On account of the ease with which mercuric oxide parts with its oxygen, it is an active oxidizing agent The yellow oxide is more active than the red, probably owing to its finer state of subdivision Hence, the yellow oxide was used in preference to the red in preparing chlorine monoxide and hypochlorous acid

§ 5 The Magnesium-Zinc Family of Elements

```
 Be
  |
 Mg
 / \
Ca  \
 |  Zn
Sr  |
 |  Cd
Ba  |
    Hg
```

These elements form a family related in many ways with one another, and with the metals of the alkaline earths. Beryllium and magnesium form a kind of subgroup, zinc, cadmium and mercury form another subgroup The metals beryllium and magnesium appear to link the alkaline earths with zinc, cadmium and mercury The scheme indicated in the margin is sometimes used to illustrate the idea There may be a missing member between cadmium and mercury, since cadmium is much more closely related to zinc than it is to mercury The vapours of all the elements appear to be composed of monatomic molecules The chemical relations have been discussed in what precedes, the physical properties of the metals are summarized in the table —

TABLE XXI —PHYSICAL PROPERTIES OF THE MAGNESIUM-ZINC METALS

—	Beryllium	Magnesium	Zinc.	Cadmium	Mercury
Atomic weight	9.1	24.32	65.37	112.40	200.0
Specific gravity	1.64	1.75	6.9–7.2	8.6	13.6
Atomic volume	5.5	13.8	9.34	13.0	15.4
Melting point	over 960°	632°	418.2°	320.2°	−38.85°
Boiling point	—	1120°	916°	780°	357.3°

The metals are not oxidized so readily as the alkaline earths. The affinity of the metals for oxygen decreases with increasing atomic weight. Beryllium does not bear so close a relationship to magnesium, zinc, and cadmium, and, while mercury has a great many similarities, it has many important differences, thus (1) The salts are all volatile; (2) it does not readily combine with oxygen; (3) its hydroxide is difficult to make; (4) the black sulphide is virtually insoluble in nitric acid; and (5) it forms two chlorides one of which resembles silver chloride. As a matter of fact, the properties of the mercuric salts can scarcely be said to fraternize very closely with the salts of any other metal.

The carbonates of these elements break up when heated into carbon dioxide, and a residual oxide, and, with the exception of magnesia, the oxides are but sparingly soluble in water. Magnesium oxide is white; zinc oxide is white when cold, yellow when hot; cadmium oxide is yellow when cold; and mercuric oxide is red. The oxides and hydroxides are soluble in solutions of ammonium salts. The basic character of the hydroxides decreases with increasing atomic weight. The hydroxides are not made by direct union of the oxide with water, and the water is easily expelled from the hydroxides by heat. This is not the case with the hydroxides of the alkaline earths. The sulphates are soluble and zinc and magnesium sulphates are isomorphous; the sulphates are all less stable than those of the alkaline earths, and their stability decreases with increasing atomic weight. The sulphates all combine with potassium sulphate—*e.g.* $ZnSO_4.K_2SO_4.6H_2O$. The chlorides are all volatile deliquescent solids; zinc and magnesium chlorides are readily hydrolyzed in aqueous solution, and form basic salts when the solutions are evaporated to dryness. This is not the case with cadmium and mercuric chlorides. The two latter readily combine with ammonia to form complex salts, and cadmium like mercury forms a lower oxide and chloride; the iodides of these two elements are isomorphous. The halides become less stable on passing from beryllium to mercury. The sulphides increase in stability and are less soluble as the molecular weight increases. The sulphides of the first two elements are not formed in the presence of water; zinc sulphide is stable in aqueous and slightly acidic solutions; cadmium sulphide is dissolved by concentrated but not by dilute acids; whereas mercuric sulphide is scarcely attacked, even by boiling nitric acid.

Questions

1. State any facts known to you which tend to show that some alloys are compounds and not mere mixtures of the constituent metals.—*London Univ.*

2. One litre of mercury vapour at the standard temperature and pressure weighs 8.923 grams. On heating 118.3938 grams of mercuric oxide, Erdmann and Marchand obtained 109.6308 grams of mercury. On the assumption that mercuric oxide is formed by the union of one atom of mercury with one atom of oxygen, what light do these facts throw on the atomic and molecular weights of mercury?—*Science and Art Dept.*

3. How is potassium chloride converted into (1) caustic potash, (2) potassium chlorate? Starting from carnallite, the double chloride of magnesium and potassium, show briefly how the metals magnesium and potassium can be obtained. —*Owens Coll.*

4. How can mercuric and mercurous chloride be obtained from mercuric sulphate? What is the action of mercuric chloride solution with solutions of (*a*) potassium iodide, (*b*) stannous chloride, (*c*) ammonia, (*d*) sodium hydroxide? —*London Univ.*

CHAPTER XIX

THE ALKALI METALS

§ 1 Potassium and Sodium Carbonates

THE ash of wood, not coal, contains about 30 per cent of potassium carbonate In special districts it may be profitable to burn wood in pits and extract the ashes with water in wooden tubs The clear liquid is evaporated to dryness in iron pots and calcined to burn away the organic matter The residue is the so called American *potash*, that is, pot-ashes Instead of evaporating the aqueous extract to dryness, a purer product can be obtained by evaporating the liquid until the less soluble impurities crystallize out, and finally evaporating the mother liquid to dryness as before White refined potash is sometimes called *pearl ash* Potash is also obtained from the residue left after beet sugar has been fermented, and the alcohol removed by distillation The liquid in the retort is evaporated to dryness, calcined, and extracted with water as before

The potash found in plants is obtained from the soil, and the potash in the soil is one product of the decomposition of rocks which form the earth's crust. The potash which herbivorous animals—*e g* sheep—draw from the land is largely exuded as an oily sweat from the skin, and called, after the French, *suint* The suint accumulates in the wool so that it may form as much as one third the weight of raw merino wool The liquid in which wool is first washed contains most of the suint This liquid can be evaporated to dryness and heated in iron pots or retorts Potassium carbonate is extracted from the residue by lixiviation with water as indicated above Most of the potassium carbonate in commerce is manufactured from potassium sulphate by Leblanc's process, to be described later

Potassium carbonate exhibits the typical alkaline reaction, for it turns red litmus blue, but, like calcium carbonate, it is a salt, and is formed by the union of the base potassium oxide, K_2O, with carbon dioxide, CO_2 When treated with an acid, the carbon dioxide is expelled, and another salt is formed. Thus with hydrochloric acid $K_2CO_3 + 2HCl = 2KCl + CO_2 + H_2O$

The alkaline lakes of Nevada and South California give sodium carbonate on evaporation "Natural soda," also called *trona* or *urao*, has been extracted commercially at Queen's lake Trona from that district has a composition corresponding with $Na_2CO_3\ NaHCO_3\ 2H_2O$

Historical —While the ashes of land plants furnish potassium carbonate, the ashes of sea plants furnish a similar, but not identical, alkali—sodium carbonate Both sodium and potassium carbonates were once included

under the Arabian term alkali. In order to distinguish these two salts from ammonium carbonate, they were termed fixed alkalies, and ammonium carbonate was called volatile alkali H L Duhamel du Monceau (1736) first clearly recognized the difference between potash and soda, and the two were distinguished by using the term vegetable alkali for potassium carbonate, and mineral alkali for sodium carbonate When M H. Klaproth (1796) showed that the vegetable alkali occurred in many minerals, the term *potash* (English), or *potasse* (French), was applied to this particular compound The Germans use the term *kali*—derived from the Arabian term "kali," for ash Klaproth also proposed to confine the term *natron* to mineral alkali, sodium carbonate The English equivalent for natron is *soda*, and the French *soude* The Italians applied the word "soda" to an ash used in making glass, and the French applied the term "soude" to the plant glasswort, the ashes of which were used in making glass and soap The first letter of the word "kali" is used by all chemists as the symbol for potassium, and the first two letters of the word "natron" for sodium

The early chemists reserved the term earth for those substances which were insoluble in water and which did not undergo alteration when calcined at a high temperature—*e g* alumina, silica, magnesia, lime, etc The earths—lime and magnesia—which were related to the alkalies by giving an alkaline reaction and neutralizing acids, were termed alkaline earths Baryta and strontia were afterwards included among the alkaline earths

§ 2 Potassium and Sodium Hydroxides

Preparation—*Sodium and potassium hydroxides* cannot be conveniently made by calcining the corresponding carbonate and digesting the residue with water as in the case of calcium hydroxide, because the two alkali carbonates do not decompose so readily as calcium carbonate The preparation of the oxides of potassium and sodium is rather difficult and expensive Hence, although the hydroxide can be made by the action of water on these oxides, it is far more economical to employ other methods of preparation Two processes are used in the manufacture of these hydroxides. Take potassium hydroxide as a type for both When calcium hydroxide is added to a boiling solution of potassium carbonate in an iron or silver or nickel vessel, calcium carbonate is precipitated, and potassium hydroxide, KOH, remains in solution $Ca(OH)_2 + K_2CO_3 = 2KOH + CaCO_3$ The clear solution is decanted from the precipitated calcium carbonate, and concentrated by heating it in iron pots The electrolysis of an aqueous solution of potassium chloride furnishes chlorine gas (*q v*), and a solution of potassium hydroxide The latter is concentrated by evaporation In Acker's process (*q v*) fused chloride is used in place of an aqueous solution

Theory of preparation—molecular—The reaction between potassium carbonate and calcium hydroxide has many points of interest It is best studied in the light of the theory of equilibrium, so useful in the study of chemical reactions generally The four salts in solution are in equilibrium, and accordingly, the reaction is represented

$$K_2CO_3 + Ca(OH)_2 \rightleftharpoons CaCO_3 + 2KOH$$

An excess of solid calcium hydroxide is supposed to be present at the start so that as fast as calcium hydroxide is removed *from* the solution by reacting with the potassium carbonate, more passes *into* solution. Thus the concentration of the calcium hydroxide in the solution is kept constant. The solubility of calcium carbonate is very small, and, in consequence, any calcium carbonate in excess of the solubility constant will be precipitated as fast as it is formed. The reaction proceeds steadily from left to right because, all the time, calcium hydroxide steadily passes into solution, and calcium carbonate is steadily precipitated. But the solubility of calcium carbonate steadily increases with increasing concentrations of potassium hydroxide. There is a steady transformation of the potassium carbonate into potassium hydroxide in progress. The concentration of the potassium carbonate is steadily decreasing, while the concentration of the potassium hydroxide is steadily increasing. Consequently, when the potassium hydroxide has attained a certain concentration so much calcium carbonate will be present in the solution that the reaction will cease. Hence the concentration of the potassium carbonate should be such that it is all exhausted before the state of equilibrium is reached. If the concentration of the potassium hydroxide should exceed this critical value, the reaction will be reversed, and calcium carbonate will be transformed into calcium hydroxide.

Theory of preparation—ionic.—The explanation offered by the ionic theory runs somewhat as follows. At the start, the solution contains the ions

$$K_2CO_3 \rightleftharpoons 2K^{\cdot} + CO_3'', \text{ and } Ca(OH)_2 \rightleftharpoons Ca^{\cdot\cdot} + 2OH'$$

The solubility product $[Ca^{\cdot\cdot}][CO_3'']$ is very small, and very much less than the solubility product $[Ca^{\cdot\cdot}][OH']^2$, consequently, since relatively large proportions of both the ions $Ca^{\cdot\cdot}$ from the $Ca(OH)_2$, and CO_3'' from the K_2CO_3 are present in the solution, calcium carbonate will be precipitated, and will continue being precipitated so long as the potassium carbonate and calcium hydroxide can supply ions CO_3'' and $Ca^{\cdot\cdot}$ in excess of the solubility product of calcium carbonate. But the calcium hydroxide furnishes the $Ca^{\cdot\cdot}$ ions, and the solubility of $Ca(OH)_2$ is determined, as we have seen, by the solubility product $[Ca^{\cdot\cdot}][OH']^2$. With the steady removal of $Ca^{\cdot\cdot}$ and CO_3'' ions, the concentration of the $K^{\cdot}$ and the OH' ions must be continually increasing. By-and-by the concentration of the OH' ions becomes relatively large; this, in virtue of the common ion OH', reduces the concentration of the $Ca^{\cdot\cdot}$ ions required to maintain the solubility product of calcium hydroxide up to its own constant value. Finally, when the concentration of the OH' ions is so great that the concentration of the $Ca^{\cdot\cdot}$ ions from the calcium hydroxide is no greater than the concentration of the $Ca^{\cdot\cdot}$ ions required to maintain the solubility product of the calcium carbonate at its own characteristic value, the reaction will stop. Hence the concentration of the potassium carbonate in the solution should be so adjusted that this salt is exhausted before the reaction stops.

Properties.—Both hydroxides are white crystalline compounds which rapidly absorb moisture and carbon dioxide from the atmosphere. In aqueous solution, both hydroxides are corrosive bases. Both compounds dissolve in water with the evolution of much heat. Both hydroxides melt easily, and are frequently cast into sticks for convenience in use. Large quantities of sodium hydroxide—also called *caustic soda*—

are used in bleaching dyeing, and in refining of oils, in the manufacture of hard soap, and of paper Potassium hydroxide—also called *caustic potash*—is also used for making soft soap

§ 3. Black's Investigation on the Carbonates of the Alkalies and Alkaline Earths

J Black's "experiments upon magnesia alba, quicklime, and other alcaline substances," published in 1755, first made clear the relations between caustic alkali and mild alkali,[1] that is, between the alkali oxides and alkali carbonates These relations were not understood by the early chemists. They believed the "mild alkalies" and "mild earths" to be elementary substances, that the causticity of lime was due to the union of "fire-matter" (phlogiston) with the element chalk, and the conversion of mild alkali into caustic alkali, with the simultaneous regeneration of chalk, by boiling the former with caustic lime, was due simply to the transfer of the "fire matter" from the lime to the mild alkali Otherwise expressed

$$\text{Quicklime} = \text{Chalk} + \text{Fire matter}$$

Black proved this hypothesis to be untenable

Black demonstrated experimentally that chalk after ignition neutralized the same quantity of acid as before ignition, but the calcined chalk dissolves in the acid without effervescence, whereas the original chalk lost a gas which he called "fixed air," but which is now called "carbon dioxide" The salts formed by the action of acids on calcined and uncalcined lime are identical in every respect, and the same amount of gas is expelled from chalk whether the chalk be calcined or digested in acids Further, by weighing the chalk before and after calcination, Black found a *loss*, not a gain, in weight Thus

Ordinary chalk	120 grains
Quicklime	68 "
Loss in weight	52 "

Hence added Black, "we may safely conclude that the volatile matter lost during the calcination is mostly air, and hence calcined lime does not emit air or make an effervescence when mixed with acids" Again, lime becomes caustic owing to the loss of fixed air Consequently Black proved

$$\text{Chalk} = \text{Quicklime} + \text{Fixed air}$$

Hence, quicklime is simpler than chalk or limestone

On boiling the 68 grains of quicklime obtained in the experiment cited above, with pot-ashes, Black finally obtained 118 grains of a white powder "similar in every trial" to ordinary chalk The 118 grains of chalk correspond with the 120 grains originally taken within the limits of experimental error The resulting caustic pot-ashes no longer effervesced with acids, whereas the regenerated chalk did Hence Black concluded that the pot-ashes were made caustic by the transfer of the gas contained in pot ashes to the caustic lime

Black thus demonstrated the modern view of the changes which attend

[1] The term "mild alkalies" was formerly applied to what are now called "alkali carbonates"

the transformation of a mild into a caustic alkali, and proved that these changes are similar to those which occur during the conversion of a mild earth into a quicklime Black's experiments also made clear the relations between the "mild alkalies" (alkali carbonates), "caustic alkalies" (alkali hydroxides), "mild earths" (carbonates of the alkaline earths), and the "quicklimes" (oxides of the alkaline earths) These interesting experiments by Black involved the use of the balance, and the method, later on, was extended by Lavoisier in his brilliant work on oxidation and combustion

§ 4 Metallic Sodium and Potassium

> When any apparently exceptional or new substance is encountered, the chemist is guided in his treatment of it by analogies which it seems to present with previously known substances —W S JEVONS

Discoveries in science are very often made by following up hints received from analogies The isolation of the metals potassium and sodium is a good illustration At the beginning of the nineteenth century, the so-called alkalies and alkaline earths—magnesia, lime, and potash—were considered to be elementary substances Lavoisier proved that some things resembling the earths—*e g* tin oxide, iron rust, mercuric oxide—could be resolved into two substances, oxygen and a metal By analogy, it was inferred that it might be possible to resolve the alkalies and the alkaline earths into the corresponding metals and oxygen After it had been shown that the electric current could resolve water and certain other salts into their elements, H Davy tried if the electric current would work in an analogous manner on caustic soda and caustic potash As a result, Davy isolated the metal potassium on October 6, 1807, and sodium a few days afterwards This discovery was soon followed by the isolation of barium, strontium, and calcium By analogy, it was further inferred that all amorphous powders—alumina, magnesia, etc —possessing similar properties, were metallic oxides As a result, when a new earth is now discovered, chemists believe, by faith, that it is the oxide of a metal even in cases where the supposed metal has never been isolated

Davy exposed a piece of solid potassium hydroxide to the atmosphere for a few seconds so that a conducting film of moisture formed on the surface The piece of potash was then placed on an insulated disc of platinum connected with the negative pole of a battery, and a platinum wire connected with the positive pole was brought in contact with the upper surface of the potash Davy adds

> Under these circumstances a vivid action was observed to take place The potash began to fuse at both its points of electrification There was a violent effervescence at the upper surface, at the lower, or negative surface, there was no liberation of elastic fluid, but small globules having a high metallic lustre and being precisely similar in visible character to quicksilver, appeared, some of which burnt with explosion and bright flame as soon as they were formed and others remained, and were merely tarnished, and finally covered by a white film which formed on their surface These globules, numerous experiments soon showed to be the substance I was in search of, and a peculiar inflammable principle, the basis of potash

Soon after Davy's discovery, J L Gay-Lussac and L J Thénard (1808) prepared the metal by heating metallic iron with potash at a white heat $4KOH + 3Fe = Fe_3O_4 + 2H_2 + 4K$. The potassium metal vaporized,

and condensed in a copper receiver containing rock oil to prevent the oxidation of the metal Later on, M Curaudau (1808) substituted charcoal in place of iron as reducing agent, and later still, H Y Castner (1888) used iron carbide—FeC_2 Calcium carbide, CaC_2, has also been used for the same purpose $6KOH + 2CaC_2 = 6K + 2CaO + 4CO + 3H_2$ The element is also obtained by the action of carbon on potassium carbonate at a high temperature $K_2CO_3 + 2C = 2K + 3CO$, but if the vapour of the potassium be not rapidly cooled, a black explosive compound with the carbon monoxide, CO, is said to be formed—potassium carbonyl, $K_2(CO)_2$ In modern works, where cheap electrical energy is available, modifications of Davy's original process—electrolysis of fused sodium hydroxide—are used for preparing sodium industrially, *e.g* H Y Castner's electrolytic process (1890) Sodium chloride mixed with powdered lead, and heated red hot in a closed retort is said to give metallic sodium $2NaCl + Pb \rightarrow 2Na + PbCl_2$

H Y Castner's electrolytic process for sodium —The sodium hydroxide, contained in an iron pot set in brickwork, is melted by means of a ring of gas jets placed underneath, and kept about 20° above the melting point (310°) of sodium hydroxide. The cathode *H*, rises through the bottom of the iron pot, *A*, Fig 134, and is maintained in position by a cake, *K*, of solid sodium hydroxide in the lower part of the pot The anodes, *F*, several in number, are suspended around the cathodes from above A cylindrical vessel, *ND*, floats in the fused alkali above the cathode, and the sodium and hydrogen liberated at the cathode collect under this cylinder The hydrogen escapes through the cover, and the atmosphere of hydrogen in the cylinder protects the sodium from oxidation A nickel wire cage, *M*, separates the anode, *F*, from the cathode, *H* From time to time the sodium, *D*, is skimmed off by means of a perforated ladle which retains the liquid metal, but allows the molten hydroxide to flow back The oxygen liberated at the anode escapes *viâ* the vent *P* Hydrogen is a by-product in Castner's process, and if there be no commercial demand for this gas, its production represents so much wasted energy Attention has been previously directed to the preparation of sodium by the electrolysis of fused sodium chloride whereby sodium is produced at one electrode, and chlorine at the other

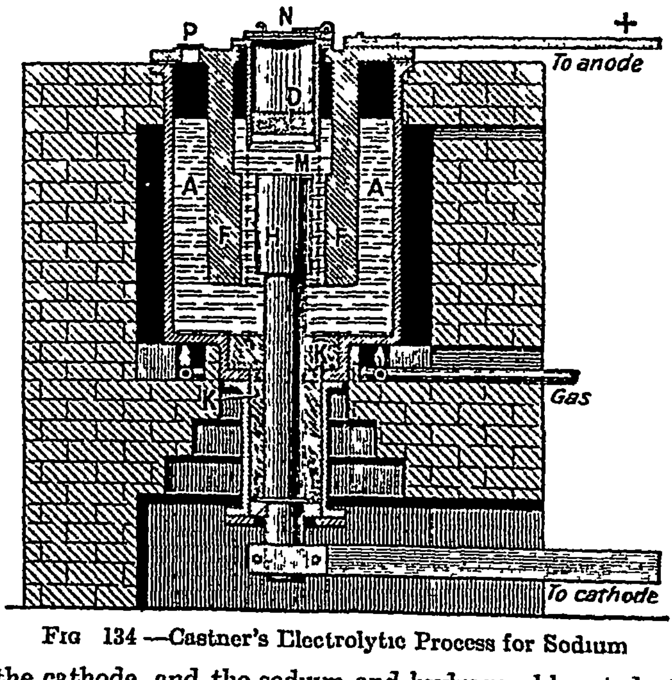


Fig 134 —Castner's Electrolytic Process for Sodium

Properties.—Both sodium and potassium are silvery white, lustrous metals which tarnish at once when exposed to the air owing to the formation of a film of oxide. These metals are therefore usually preserved in well-stoppered vessels, or in a liquid containing no oxygen, *e.g.* naphtha, or petroleum. In thin layers on glass, potassium appears bluish violet; sodium, yellowish-brown. The vapour of potassium at a red heat appears to be violet, and sodium colourless in thin layers, purple in thick layers. The metals are lighter than water, and at ordinary temperatures they are soft enough to be moulded between the fingers. Sodium melts at 97°, potassium at 62.3°; sodium boils at 877.5°, potassium at 700°. Potassium is rather more chemically active than sodium. Both metals react with water to form hydroxides: $2K + 2H_2O = 2KOH + H_2$. The heat of the reaction with potassium suffices to ignite the hydrogen; with sodium, the hydrogen ignites if the water is warmed. The flame of hydrogen is coloured by the vapours of the respective metals—potassium, lavender-blue; sodium, daffodil yellow. Both metals dissolve in liquid ammonia, giving blue solutions; with potassium the solution is indigo blue. Heated in an atmosphere of carbon dioxide, free carbon and a carbonate of the metal are formed. Potassium with carbon monoxide forms the explosive compound previously mentioned; with the halogens, the metals take fire, forming the corresponding halides; when heated in hydrogen, white crystalline hydrides are formed—KH and NaH; and in air, sodium and potassium burn, each metal forming a mixture of oxides. Perfectly dry air or oxygen has no appreciable effect upon the dry metals.

Uses.—An alloy of potassium and sodium, liquid at ordinary temperatures, is used for some high temperature thermometers above the boiling point of mercury. Sodium is used in the manufacture of sodium cyanide and sodium peroxide, in drying oils, and in the manufacture of organic compounds.

Atomic and molecular weights.—The combining weight of sodium determined by the analysis of sodium salts—sodium chloride, etc.—lies between 23.00 and 23.17; the best representative value is probably 23. The atomic weight by Dulong and Petit's method of approximation ($6.4 \div$ specific heat $=$ atomic weight) is $6.4 \div 0.283 = 22.6$. Consequently, 23 is taken to be the atomic weight of sodium. The vapour density of sodium is 25.7, which corresponds with a one-atom molecule. Similarly, analyses of potassium chloride and other potassium salts show that the combining weight of potassium lies between 38.67 and 39.33; the best representative value is supposed to be 39.10; and, the specific heat being 0.166, Dulong and Petit's method of approximation furnishes $6.4 \div 0.166 = 38.56$, corresponding with the atomic weight 39.10. The vapour density 42.34 at 1040° corresponds with a one atom molecule. Freezing-point determinations of solutions of the metals in mercury show that these elements have a one atom molecule when dissolved in mercury. The vapour densities of potassium and sodium chlorides at 2000° show that here again the atomic weights of potassium and sodium are probably 39.10 and 23 respectively.

Occurrence.—Potassium and sodium only occur in nature combined with other elements, but the compounds are widely distributed, being present in many silicate rocks, etc. Potassium occurs as sylvine, carnallite, kainite, etc., in the Stassfurt deposits (*q.v.*). Sodium is present in sea water, etc., and it occurs as rock salt (*q.v.*) and as Chili saltpetre (*q.v.*).

§ 5 Potassium and Sodium Monoxides and Peroxides

Sodium and potassium monoxides—Na_2O and K_2O—The monoxides of the alkali metals are made by heating the metals in a limited supply of dry air at a temperature below 180°, and removing the excess of metal by distillation in vacuo The monoxides so obtained are not pure, being probably a mixture of monoxide, say Na_2O, and peroxide, Na_2O_2 The monoxides have also been made by heating the metal with the corresponding nitrates $2NaNO_3 + 10Na = 6Na_2O + N_2$. The two oxides combine with water to form the hydroxides with the evolution of a considerable amount of heat Lithium oxide, however, does not evolve so much heat

Sodium peroxide, Na_2O_2—This oxide is formed when sodium is burnt in a stream of oxygen, or when the metal is heated in aluminium trays in iron tubes at about 300° The product contains about 95 per cent of sodium peroxide Pure sodium peroxide is white, but the commercial product is usually tinged yellow The peroxide is stable in dry air at ordinary temperatures, and in moist air, or in the presence of water, it is decomposed with the evolution of oxygen and the formation of sodium hydroxide $2Na_2O_2 + 2H_2O = 4NaOH + O_2$, but if the temperature be kept low, hydrogen peroxide is formed $Na_2O_2 + 2H_2O = 2NaOH + H_2O_2$ A hydrate, $Na_2O_2 8H_2O$, has been prepared Sodium peroxide is a powerful oxidizing agent, and it is used in the laboratory for oxidizing purposes and also for decomposing silicate rocks prior to analysis Sodium peroxide is also used in straw bleaching, etc

Potassium tetroxide, K_2O_4—This oxide is formed as a chrome-yellow powder when metallic potassium is melted in an atmosphere of nitrogen, and the nitrogen is gradually displaced by air or oxygen It is also formed when potassium is heated in nitrous oxide, N_2O If the temperature be suitably regulated, K_2O_2 is said to be formed, but there is some doubt about this When treated with water, potassium tetroxide forms potassium hydroxide, hydrogen peroxide, and oxygen, when heated with carbon monoxide, potassium carbonate and oxygen are formed $K_2O_4 + CO = K_2CO_3 + O_2$

§ 6 Spectrum Analysis.

> If there ever was a flank movement on Nature by which she has been compelled to surrender a part of her secrets, it was the discovery of the spectroscope, which enables us to peer into the very heart of Nature —R C KEDZIE

Isaac Newton (1666) proved experimentally that a beam of sunlight is composed of light rays of various colours perfectly blended and ranging from red through orange, yellow, green, and blue to violet This Newton did by passing the beam of sunlight through a glass prism, and projecting the beam on to a screen, Fig 135 The violet, green, and blue rays are bent more in passing through the prism than the yellow, orange, and red rays The beam of light after passing through the prism thus appears on the screen as an unbroken band of colours, which is called a continuous spectrum Any beam of "white" light can be used in place of sunlight, for instance, the light from an incandescent solid such as the limelight, Welsbach's mantle, incandescent carbon, etc W H Wollaston (1802) noticed that the beam of sunlight really furnished a spectrum which is crossed

by a large number of dark lines—some sharp and well defined, others more or less faint and nebulous J von Fraunhofer (1814–15) carefully mapped the relative positions of a number of these dark lines, and accordingly they are now generally called Fraunhofer's lines It was also shown that incandescent vapours and gases furnish a discontinuous or line spectrum, that is, a spectrum composed of a few bright lines instead of a continuous band. The line spectra of some elements are comparatively simple, for they display but a few clear distinct coloured lines—*e.g* sodium a yellow line, thallium a green line, indium a blue and an indigo line Other elements have complex spectra containing numerous lines of varying intensity—*e.g* barium, strontium, iron The spectra of some elements, though complex, are easily recognized by the prominence and position of

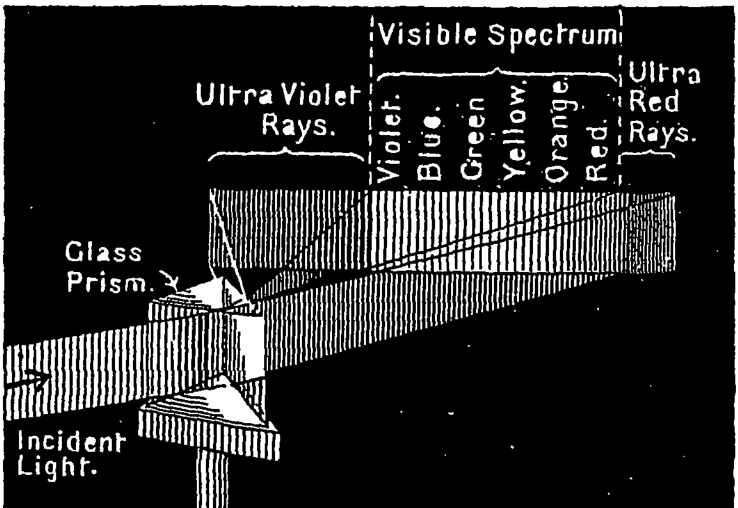


FIG 135 —Newton's Experiment

certain lines—*e g* the dark red line of rubidium, the blue line of cæsium, etc

It was provisionally assumed that "Fraunhofer's lines are due to the lack of certain shades of colour in the spectrum of sunlight" This plausible hypothesis was tested by L. Foucault in 1849 He arranged an experiment in which a ray of sunlight was directed by means of lenses on to the glowing gases between the poles of an arc light which alone gave a spectrum with two yellow lines very prominent The mixed light was passed through a prism. Foucault expected the lacuna in the solar spectrum corresponding with the yellow lines of the glowing gases in the arc light would be filled by the latter, and that the yellow portion of the solar spectrum would be continuous To his astonishment, the reversed or dark lines of the solar spectrum corresponding with the bright yellow lines were more pronounced than before Hence the preliminary hypothesis cannot be true

Foucault then suggested the hypothesis that "the incandescent gases in the arc light have the power of absorbing the yellow from sunlight, as

well as of emitting yellow light The increase in the darkness of these lines is due to this absorbing power being greater than the emissive power" Foucault focussed the light from an incandescent carbon—which by itself gives a continuous spectrum—on to the incandescent gases between the carbon poles Instead of getting the continuous spectrum of the incandescent carbon with yellow lines enhanced by the spectrum of the gases between the carbon poles, Foucault obtained a spectrum with the dark lines in the yellow portion This experiment supported his hypothesis, and had Foucault known that the yellow lines were due to sodium he would have recognized the origin of Fraunhofer's lines This step was taken by G Stokes, 1852 In 1859 R Bunsen and G Kirchhoff definitely settled the question The subsequent history of spectrum analysis is but an illustration of the fact that once the right explanation of a phenomenon is found, the facts seem to arrange themselves about the theory as naturally as the particles of a salt in a solution aggregate about the enlarging nucleus of a crystal

Bunsen and Kirchhoff proved that (every element produces its own characteristic spectrum , and reciprocally, the presence of the vapour of an element can be inferred with certainty when the characteristic lines are present) The spectrum of the incandescent vapour of a mixture of elements contains all the lines characteristic of each element in the mixture, and consequently it is possible to recognize each and all of them by measuring the position of the bright lines and comparing the lines with those of known elements This method of detecting elements is called spectrum analysis Bunsen and Kirchhoff were able to prove that the dark Fraunhofer's lines are due to the rays of light from an incandescent solid passing through vapours of various elements In other words, Fraunhofer's lines are due to the rays of light from an incandescent sun passing through the sun's atmosphere, and consequently the vapours of the elements whose line spectra correspond with the dark lines of the solar spectrum must be present in the sun's atmosphere

By the aid of spectrum analysis, therefore, it has been possible to deduce the presence of a large number of known elements—some 34—in the sun's atmosphere from the coincidence of the bright lines furnished by elements in the laboratory with the dark lines in the solar spectrum. The halogen elements, nitrogen, oxygen, gold, mercury, and a few other elements, have not been detected in the sun The spectrum of an unknown element—helium—was observed in the solar spectrum some thirty years before the corresponding element was discovered in the earth The light from the fixed stars furnishes results similar to those obtained with sun light The lines of hydrogen, helium, carbon, magnesium, calcium, and iron have been detected in nebulæ, and hydrogen and hydrocarbons have been recognized in comets

The spectroscope —Quite a large number of instruments have been devised for the examination of the spectra of different substances The so-called direct vision spectroscopes have a slit at one end to admit the light under examination The slit can be narrowed or widened by turning a suitable screw The beam of light passes from the slit through a prism, and is thence directed to the eye piece where it is examined

The spectra of solids and liquids —Solids and liquids must be vaporized before their spectra can be examined It is often sufficient to

introduce salts of the elements into a non luminous Bunsen's flame by means of a clean platinum wire The flame spectrum is then examined by means of the spectroscope This method is satisfactory provided there is plenty of material, and the salt volatilizes and dissociates in the flame If the substance is not volatilized in the Bunsen's flame, or if but a minute quantity of the substance is available, it is best to use a spark spectrum obtained in the following manner—due to Delachanel and Mermet A test tube, Fig 136, has a platinum terminal fused into the bottom to serve as one electrode, a cork in the mouth of the test-tube supports a glass tube pierced with a platinum wire to serve as the other electrode The height of the solution in the test-tube is arranged so that a certain portion rises by capillarity and fills a central cavity in the glass tube holding the lower electrode When the cup is full, every time a spark passes a very minute portion of the solution is vaporized, no material is lost, and the uniformity of the volatilization with each spark permits continuous observations

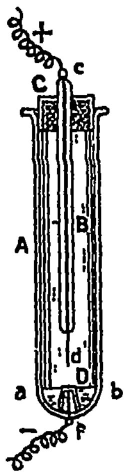


Fig 136 — Spectrum Tube Liquids

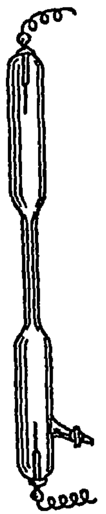


Fig 137 — Spectrum Tube Gases

The spectra of gases—The spectrum of a gas is obtained by sealing the gas in a tube, Fig 137, while the gas is under a reduced pressure Each end of the tube has a platinum wire sealed into it, and these wires are put in communication with an induction coil When a series of sparks are passed through the gas, the gas becomes incandescent, particularly in the narrowed portion of the tube, and the characteristic spectrum for that particular gas is obtained

It might be added that the spectrum of a gas depends partly upon the *pressure* under which the gas is confined At small pressures, spectra with broad bands are obtained As the pressure is increased, "new series of lines arise which only existed in germ at lower pressures", the bands give way to lines, and finally a continuous band of light is obtained corresponding with the pure spectrum. The character of the lines also depends upon the *temperature* under which the gas or vapour is examined Sodium in a Bunsen's flame, for instance, gives one well defined yellow line which is really compounded of two yellow lines, but at higher temperatures, three other pairs of lines make their appearance

Absorption spectra—Some substances absorb certain colours and transmit others If coloured solutions are examined by the spectroscope illuminated by the light of an incandescent solid transmitted through the solution, a series of dark bands or lines called absorption spectra are obtained. A number of solutions have very characteristic absorption spectra—*e g* blood, didymium chloride, copper sulphate, potassium chromate, potassium permanganate, potassium dichromate, etc

The delicacy of spectrum analysis—The spectroscope is one of the most delicate means of detecting many substances, and it enables elements

to be recognized with certainty when present in quantities far too small to produce an appreciable effect upon the most sensitive reagents known Thus 1 c c of air contains approximately 0 0001 c c of neon, and the neon in $\frac{1}{20}$ c c of ordinary air, that is, 0 000005 c c of neon has been detected by means of the spectroscope By means of the spectroscope also it is possible to detect the presence of 0 00006 milligram of strontium and of calcium, 0 00001 milligram of lithium, and 0 0000003 milligram of sodium It is not likely that rubidium and cæsium would have been discovered so soon had it not been for their striking spectra Thallium, indium, and gallium were also discovered by the aid of the spectroscope

§ 7 Lithium, Rubidium, and Cæsium

Lithium, Li—The three elements—lithium, rubidium, and cæsium—are related to potassium and sodium Lithium was discovered by A Arfvedson, in 1817 The name lithium is derived from the Greek λίθεος (litheos), stony, because it was believed, at the time of its discovery, that its presence was confined to the mineral kingdom Lithium is widely distributed in small quantities It occurs in a number of minerals. *lepidolite*, or lithia mica, contains up to about 6 per cent of lithia, *spodumene*—$Li_2O\ Al_2O_3\ 4SiO_2$—up to about 6 per cent, and *petalite* has up to about 3 per cent of lithia Lithium has been detected in sea water and in most spring and river waters W A Miller (1864) has reported 0 37 gram per litre in the water of a mine at Redruth (Cornwall) Lithium has also been detected in the ash of many plants—tobacco, sugar cane, etc, in the ash of milk, blood, etc, and also in a number of meteorites

To extract lithium, the powdered mineral is calcined with a mixture of ammonium chloride and calcium carbonate The aqueous extract is treated with hydrochloric acid and evaporated to dryness The lithium chloride is extracted with amyl alcohol or pyridine in which the lithium chloride is fairly soluble

When the solution of the chloride is treated with ammonium carbonate, lithium carbonate, Li_2CO_3, is precipitated Lithium carbonate, unlike the other alkaline carbonates, is decomposed at a high temperature, and in this respect resembles the carbonates of the alkaline earths The metal is made by the electrolysis of the fused chloride The metal resembles sodium and potassium It decomposes water, but the hydrogen does not ignite even if the water be boiling When heated in air, the metal forms lithium monoxide, or lithia, Li_2O, but it does not readily form a higher oxide Lithium metal unites rapidly with hydrogen at a red heat, forming lithium hydride, LiH, with nitrogen it forms lithium nitride, Li_3N Lithium carbonate and lithium phosphate, unlike the other alkaline carbonates and phosphates, are but sparingly soluble in water Lithium salts are sometimes used in the treatment of diseases due to uric acid poisoning R Bunsen and A Matthiessen prepared relatively large quantities of metallic lithium, in 1855, by the electrolysis of the fused chloride, many others appear to have obtained the metal before 1855, but in quantities too small for examination

Cæsium and rubidium—R Bunsen and G Kirchhoff (1860), while investigating the mineral waters of Durkheim (Palatinate), evaporated down 40 tons of the water, and removed the alkaline earths, and lithia

1928.

with ammonium carbonate The filtrate showed the spectral lines of sodium, potassium, and lithium, "and besides these, two splendid blue lines" near to the blue strontium line Bunsen and Kirchhoff add

> As no elementary body produces two blue lines in this portion of the spectrum, we may consider the existence of this hitherto unknown alkaline element was thus placed beyond doubt The facility with which a few thousandths of a milligram of this body may be recognized by the bright blue light of its incandescent vapour, even when mixed with large quantities of more common alkalies, has induced us to propose for it the name cæsium (and the symbol Cs), derived from the Latin *cæsius*, used to designate the blue of the clear sky

Again, on extracting the alkalies from lepidolite (Saxony) and washing the precipitate obtained by treating the solution of the alkalies with hydrochloroplatinic acid with boiling water a number of times, the residue finally gives "two splendid violet lines" between those due to strontium and to potassium, as well as a number of other lines in the red, yellow, and green portions of the spectrum Bunsen and Kirchhoff say

> None of these lines belong to any previously known body Amongst them are two which are particularly remarkable in lying beyond Fraunhofer's line in the outermost portion of the red solar spectrum Hence we propose for this new metal the name rubidium (and the symbol Rb), from the Latin *rubidus*, which was used to express the darkest red colour

Compounds of the two elements are so like those of potassium that they cannot be distinguished from that element by the ordinary tests. The only satisfactory means of detecting the two elements is by spectrum analysis Rubidium and cæsium occur together in lepidolite, in carnallite, and in some porphyries Lepidolite does not contain a quarter per cent. of rubidia, while carnallite may contain up to 4 per cent of rubidia They also occur in many mineral waters, in sea water, in the ashes of plants The mineral *pollux*—cæsium aluminosilicate—contains the equivalent of some 34 per cent of cæsia Otherwise both elements occur in very small quantities, and somewhat widely diffused in nature If present in a mineral, both elements will be found with the alkalies after separating the other elements with ammonium carbonate, etc The residue when treated with hydrochloroplatinic acid furnishes the chloroplatinates of the alkalies. The sodium salt can be removed by washing with alcohol The three remaining elements—potassium, rubidium, and cæsium—can be separated by taking advantage of the difference in the solubilities of their alums (see "Alums") 100 c c of water at 17° dissolve 0 62 gram of cæsium alum, 2 27 grams of rubidium alum, and 13 5 grams of potassium alum In passing, it may be mentioned that the same amount of water dissolves 51 grams of sodium alum The chlorostannates—Rb_2SnCl_6 and Cs_2SnCl_6—are much less soluble in water than the corresponding potassium salt, and hence rubidium and cæsium can be separated from potassium by converting the salts into chlorostannates. Cæsium can be separated from rubidium by treatment with antimony trichloride The cæsium salt $2CsCl.SbCl_3$ is precipitated, while the corresponding rubidium salt is soluble in water

In connection with cæsium, it is interesting to note that C F Plattner, in 1846, was not able to make his analysis of the mineral pollux (from Elba) add up to 100 per cent After Bunsen had discovered cæsium, F Pisani (1864) showed that Plattner had mistaken cæsium (atomic weight 132 8) for potassium (atomic weight 39 1) By making the corresponding correction, Plattner's analysis was found to be quite satisfactory. To make this quite clear, suppose that 5 grams

of a compound, supposed to be potassium chloride, are obtained This will be multiplied by 0 631 to get the equivalent amount, 3 16 grams of K_2O, but if the compound be CsCl, not KCl, then the weight must be multiplied by 0 835 to get the corresponding amount, 4 18 grams of Cs_2O The analysis would thus appear to be 4 18 less 3 16, that is 1 02 grams too low if the 5 grams of cæsium chloride were mistaken for potassium chloride This is a remarkable tribute to the accuracy of Plattner's analysis

Metallic rubidium is prepared by heating an intimate mixture of the carbonate with finely divided carbon, metallic cæsium is prepared by heating the hydroxide with magnesium, or by electrolyzing a fused mixture of cæsium and barium cyanides The barium cyanide is added to make the mixture more fusible Both metals have been obtained by heating the chlorides with calcium in exhausted tubes The metals, their oxides and their salts, are closely kin to the salts of potassium and sodium The tendency of rubidium and cæsium to form polyhalides is characteristic.

§ 8 The Relations between the Alkali Metals.

The five elements, lithium, sodium, potassium, rubidium, and cæsium, called the alkali metals, exhibit an interesting gradation in the properties of the elements and their compounds in accord with the increase in their atomic weights, from member to member, in passing from lithium to cæsium The metals are silvery white, soft enough to be cut with a knife, rapidly tarnish in air, and decompose water at ordinary temperatures The lowest temperature at which the action of the different metals on water can be detected is —98° for sodium, —105° for potassium, —108° for rubidium, and —116° for cæsium The elements are all univalent, and manifest a remarkable affinity for oxygen, cæsium and rubidium ignite spontaneously if placed in dry oxygen at the room temperature Sodium and lithium, though compatible with the other members of the family, have feebler affinities The chemical activity of the alkali metals appears to increase steadily in passing from lithium to cæsium The gradation in the physical properties is illustrated in Table XXII.

TABLE XXII —PHYSICAL PROPERTIES OF THE ALKALI METALS

	Lithium	Sodium	Potassium	Rubidium	Cæsium
Atomic weight	6 94	23 00	39 10	85 45	132 81
Specific gravity	0 534	0 9723	0 859	1 525	1 903
Atomic volume	13 1	23 7	45 4	55 8	71 0
Melting point	180°	97 6°	65 5°	39°	28 5°
Boiling point	+1400°	877 5°	757°	696°	670°
Specific heat at 0°	0 941	0 2811	0 1728	0 0802	0 0522
Coefficient expansion	—	0 000274	0 000282	0 000338	0 000345
Heat of fusion (cals)	—	27 21	14 67	6 144	3 766

The elements have a remarkably low specific gravity, and a high atomic volume (*q v*) The oxides and hydroxides are markedly basic, they do not exhibit acidic qualities The physical properties of the salts—solubility in water, molecular volume, optical properties, and the variation in the form of the crystals show the same order of variation as the atomic weights of the elements Lithium differs in many respects from the other members

of the family The salts of the alkali metals —nitrates, chlorides, sulphides, sulphates, phosphates, carbonates, etc —are nearly all soluble in water, although lithium, carbonate, phosphate, and fluoride are very much less soluble than the corresponding salts of the other members And in this respect, lithium resembles the members of the calcium family, and it thus forms a connecting or bridge element between the alkalies and alkaline earths The alkali sulphates form isomorphous characteristic alums (*q v*), but lithium alum appears to be so soluble that it has not yet been crystallized. The modes of crystallization of sodium and potassium sulphates and carbonates are worth noting Lithium carbonate is sparingly soluble in water, sodium carbonate is not deliquescent, the others are The salts of sodium and lithium form stable hydrates with water, whereas potassium, rubidium, and cæsium salts are nearly all anhydrous Sodium resembles lithium in the solubility of its chloroplatinate, acid tartrate, and alum so much so that the alkali metals are sometimes divided into two classes (1) those with sparingly soluble chloroplatinates—viz potassium, rubidium, and cæsium, and (2) those with soluble chloroplatinates—viz sodium and lithium

§ 9 Atomic Volume.

> A connection frequently exists between physical and chemical properties, and in many cases recourse must be had to both for an explanation of a pheno menon to which they may each contribute —C L BERTHELOT (1803)

The quotient obtained by dividing the atomic weight of an element by its specific gravity in the solid condition is called the atomic volume of the element Consequently, the atomic volume represents the number of cubic centimetres occupied by an amount of the element

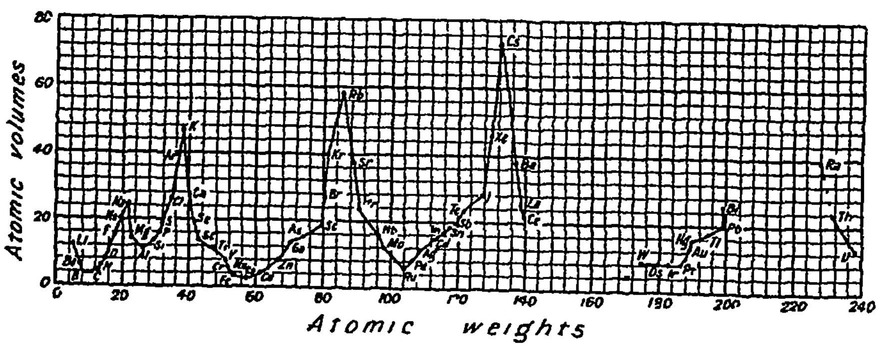


FIG 138 —Relation between Atomic Volumes and Atomic Weights

equal to its atomic weight expressed in grams The magnitude of the atomic volume thus corresponds with the looseness of texture or porosity, so to speak, of the solid element Curiously enough, when the atomic volumes of the elements are plotted with the atomic weights, a periodic curve showing a number of maximum and minimum points is obtained, as illustrated in Fig 138 The atomic volume, for instance, decreases in passing from lithium to boron, after which it increases through carbon, oxygen, and fluorine to sodium, when it again decreases through magnesium down to aluminium, and thence increases to potassium Thus the curve

passes down and up time and again A similar curve was obtained in Fig 105 for the heats of formation of the chlorides Certain portions of the curve are incomplete owing to the lack of data

The elements boron, aluminium, cobalt and nickel, rhodium, etc, occupy the troughs of the curve, while the alkali metals occupy the crests of the curve, thus corresponding with the fact that these elements have the largest atomic volumes, or the largest spaces between the atoms Presumably, the spaces between the atoms of these solid elements are relatively large compared with the size of the atoms themselves This is often taken to mean that the constituent particles of these elements approximate more nearly to the condition of the particles of a gas than other elements with small atomic volumes According to D I Mendeléeff, the chemical activity of the alkali metals is due to this circumstance, and this assumption is in agreement with the observed increase in the chemical activity of these elements in passing from lithium to cæsium

The atoms of a solid probably do not touch one another, and the volume of a solid thus includes (1) the size of the atoms as well as (2) the spaces between the atoms of the molecule, and (3) the spaces between the molecules It is not at present possible to distinguish clearly between the effects of these factors

Questions

1 What is meant by a normal solution of an acid? How many c c of a normal solution of hydrochloric acid would be required to neutralize 1 5 grammes of potassium hydroxide?—*Aberdeen Univ*

2 Define the following terms (1) Equivalent of an element, (2) equivalent of a compound, (3) gram-atom, (4) gram molecule, (5) normal solution —*Princeton University, U S A*

3 What is meant by the atomic volume of a substance? How is it determined?—*Science and Art Dept*

4 From what minerals are the salts of potassium prepared and where do they occur? How is potassium nitrate prepared from potassium chloride? How would you show the presence of potassium in a mixture of calcium, sodium, and potassium chlorides?—*Aberdeen Univ*

5 Describe two or three cases of chemical change in which the influence of "mass" is evident as a factor in the operation —*London Univ*

6 Give an account of the chief forms in which calcium carbonate is found Ten grams of quicklime are slaked, mixed to a paste with water, and added to an excess of sodium carbonate, how much caustic soda is formed (Ca = 40, Na = 23)?—*Owens Coll*

7 What is a spectrum? Describe the appearance of any spectrum which you have seen —*London Univ*

8 Name two compounds containing lithium and describe the preparation of lithium chloride from one of them In what respects do lithium compounds resemble or differ from corresponding derivatives of other alkali metals?—*Board of Educ*

9 From your knowledge of the characteristics of opposing reactions what would you expect to happen when an aqueous solution of barium hydroxide is mixed with an aqueous solution of a potassium salt?—*Aberdeen Univ*

10 Give an account of the chief forms in which calcium carbonate is found Ten grams of quicklime are slaked, mixed to a paste with water, and added to an excess of sodium carbonate How much caustic soda is formed?—*Owens Coll*

11 How is potassium chloride converted into (*a*) caustic potash, (*b*) potassium chlorate? Starting from *carnallite*, the double *chloride* of magnesium and potassium, show briefly how the metals magnesium and potassium can be prepared —*Owens Coll*

12 What is meant by (*a*) spark spectrum, (*b*) absorption spectrum, (*c*) reversed lines? How would you distinguish between the spectra of the metals of the alkaline earths?—*Cape Univ*

CHAPTER XX

ELECTRICAL ENERGY

§ 1 Electrochemical Series of the Elements.

METALLIC magnesium will displace hydrogen from dilute acids $Mg + H_2SO_4 = MgSO_4 + H_2$, or in the language of the ionic hypothesis $Mg + 2H + SO_4'' = Mg + SO_4'' + H_2$ Magnesium will also precipitate zinc from a solution of a zinc salt $Mg + ZnSO_4 = MgSO_4 + Zn$, or in terms of the ionic hypothesis $Mg + Zn + SO_4'' = Mg + SO_4'' + Zn$. Zinc in turn will precipitate iron from iron salts, iron will precipi-ate copper from copper salts, copper will precipitate silver from silver alts, etc By treating the metals in this manner, it has been found possible o arrange them in a series such that any metal in the list will usually dis lace those which follow it, and be displaced by those which precede it, thus

$$Mg \rightarrow Al \rightarrow Mn \rightarrow Zn \rightarrow Cd \rightarrow Fe \rightarrow Co \rightarrow Ni \rightarrow Sn \rightarrow Pb \rightarrow Bi \rightarrow \text{etc}$$

Again, when zinc is treated with dilute acids under suitable conditions n a voltaic cell (Fig 3), so as to eliminate disturbing effects, the reaction produces an electric current at a certain voltage If the zinc be replaced by some metals—aluminium, magnesium, etc —the voltage of the cell s increased, and conversely, if the zinc be replaced by other metals—admium, iron, cobalt, etc —the voltage of the cell is diminished It is hus possible to arrange the elements in a series representing the potential lifference in volts which is developed between the metals and solutions of heir salts.

The order here is virtually the same as the above list showing the order in which the elements displace one another from their salts The ist of the elements so arranged is called the electrochemical series A more complete list is indicated in Table XXIII

The order may vary a little with different solutions, secondary re-actions may prevent the precipitation of the metal. In many cases, the dis placement is so complete that the reaction is employed in quantitative analysis The further apart the metals in the series, the greater the amount of heat liberated when the displacement occurs, *e g* when zinc precipi-ates silver more heat is evolved than when it precipitates tin Similar emarks apply, *mutatis mutandis*, to the speed of precipitation A similar able would be obtained if the elements were arranged in the order of heir chemical activity Thus, the earlier members on the list oxidize or ust on exposure to the air, oxides of the metals succeeding manganese are reduced to metals when heated in a stream of hydrogen, while the

metals which precede manganese, under the same conditions, may be reduced to lower oxides, but not to the metallic condition. The oxides of the metals mercury to osmium may be decomposed by simply heating. (The metals preceding hydrogen on the list can give hydrogen when treated with acids, although secondary actions may simultaneously lead to the formation of some product other than hydrogen. The metals succeeding hydrogen do not usually displace hydrogen from the acids.) With the possible exception of tin and lead (metals close to hydrogen) the free elements are rarely, if ever, found in nature excepting possibly in meteorites. This arises from the fact that natural waters containing carbonic and other acids in solution attack these metals, consequently, even if these elements were produced by subterranean agents—volcanic or otherwise—they must succumb to attack by natural waters.

It will be noticed that the series only refers to the action of the *free* elements, and it has no direct reference to the mutual action of compounds of the elements upon one another. The order of the elements in the electrochemical series depends to some extent upon the temperature as well as on the nature and concentration of the electrolyte. For example, zinc and copper behave in what appears to be an abnormal manner in the presence of potassium cyanide. Thus copper and iron will precipitate zinc from potassium zinc cyanide, whereas zinc will precipitate copper from copper sulphate, and iron from neutral ferrous sulphate. Again, silver will displace hydrogen from aqueous hydriodic acid, copper will precipitate nickel from sodium nickel chloride, and platinum will liberate hydrogen from aqueous solutions of potassium cyanide.

Electro-affinity.—The idea has been expressed another way. It is assumed that the ions hold their charges with different degrees of tenacity. The ions—K˙, Na˙, NO_3', Cl′, etc.—which hold their charges very tenaciously, are called strong ions; and ions—Hg˙˙, Ag˙, OH′, Cy′, etc.—which readily lose their charge, are called weak ions. The degree of tenacity with which the ions of an element hold their charges has been called the electro affinity of the element. Ions with strong electro affinity are difficult to prepare in a free state, and

TABLE XXIII.—ELECTROCHEMICAL SERIES OF THE ELEMENTS.

Cæsium	"Metals"
Rubidium	
Potassium	
Sodium	
Lithium	
Barium	
Strontium	
Calcium	
Magnesium	
Aluminium	
Chromium	
Manganese	
Zinc	
Cadmium	
Iron	
Cobalt	
Nickel	
Tin	
Lead	
Hydrogen	
Antimony	
Bismuth	
Arsenic	
Copper	
Mercury	
Silver	
Palladium	
Platinum	
Gold	
Iridium	
Rhodium	
Osmium	
Silicon	"Non metals."
Carbon	
Boron	
Nitrogen	
Selenium	
Phosphorus	
Sulphur	
Iodine	
Bromine	
Chlorine	
Oxygen	
Fluorine	

conversely If an element with a strong electro affinity comes in contact with the ion of an element with a weak electro affinity, the charge on the latter passes over to the former Thus, zinc has a stronger electro affinity than copper, and, in consequence, as indicated above, zinc will precipitate copper from solutions of its salts $Zn + Cu = Zn + Cu$ Zinc also has a stronger electro affinity than hydrogen, and consequently zinc dissolves in dilute acids with the evolution of hydrogen $Zn + 2H = Zn + H_2$ Similarly, chlorine has a stronger electro affinity than bromine, and bromine a stronger electro affinity than iodine In consequence, chlorine will displace bromine from aqueous solutions of the bromides $Cl_2 + 2K + 2Br' \rightleftharpoons 2K + 2Cl' + Br_2$, and bromine will displace iodine from the iodides $Br_2 + 2K + 2I' \rightleftharpoons 2K + 2Br' + I_2$

§ 2 Solution Pressure—Contact Differences of Potential

Every metal, except, of course, the last in the series, will displace those that succeed it in the electrochemical series, and it is inferred as an hypothesis that each of these metals has a tendency to become ionic This tendency is hypothetically regarded as a solution pressure which drives the ions of the metals into solution This pressure must be greatest with the metals at the cæsium end, and least with the metals at the osmium end of the series Conversely, the tendency of positive metal ions in solution to reprecipitate on the negative electrode must be least at the cæsium end of the series, and greatest at the osmium end The ionic hypothesis assumes that this back or deposition pressure represents the osmotic pressure of the ions

The dissolution or ionization of a metal has been compared with the tendency of different liquids to vaporize at any given temperature Just as a liquid in a closed vessel will evaporate until the number of molecules leaving the surface of the liquid in a given time is equal to the number of molecules returning to the liquid, so W Nernst (1889) has suggested that a metal when placed in contact with water, or any other solvent, sends positively charged ions into the solvent, and itself acquires a negative charge The ionization of the metal, so to speak, is supposed to continue until the concentration of the metallic ions in the liquid has attained a certain value when a state of equilibrium ensues The number of ions passing into the solution is then equal to the number reprecipitated on the surface of the metal Direct proof of the presence of iron ions in purified water which has been in contact with the highly purified iron is wanting The evidence is indirect, or rather hypothetical

When zinc is immersed in dilute hydrochloric acid, the H ions which come in contact with the zinc plate lose their charge, and positively charged zinc ions pass into solution If a stick of metallic zinc be dipped in a saturated solution of zinc sulphate, the solution and deposition pressures are balanced, and no action occurs, but if a stick of metallic zinc be placed in a dilute, say normal, solution of zinc sulphate, the solution pressure is greater than the deposition pressure, and positively charged zinc ions pass from the zinc rod into the solution In consequence, the zinc acquires a negative charge, and the solution a positive charge, in agreement with the fact that zinc usually acquires a negative charge when immersed in a solution of its own salt. Similar remarks apply to aluminium, iron, etc

Conversely, if the solution pressure be less than the deposition pressure of the ions, as appears to be the case with a stick of metallic copper immersed in a solution of copper sulphate, copper ions will be deposited on the metal, and the solution will acquire a negative charge while the metal acquires a positive charge This also appears to be the case with the metals silver, mercury, etc

The electrical effect, or the contact difference of potential, produced when the different metals are immersed in a normal solution of their sulphates has been measured. A few of the results are here indicated.

	Volts
Magnesium	−1·214
Zinc	+0·493
Cadmium	−0·141
Hydrogen	0
Copper	−0·606
Silver	−1·048

The " + 0·493 " opposite zinc means that if metallic zinc be immersed in a normal solution of zinc sulphate, the solution will acquire a positive charge, and the metal a negative charge; and the difference of potential between the solution and the metal will be 0·493 volt With metallic copper and a solution of copper sulphate, the solution will be charged negatively and the copper positively such that the difference of potential between the solution and the metal will be 0·606 volt

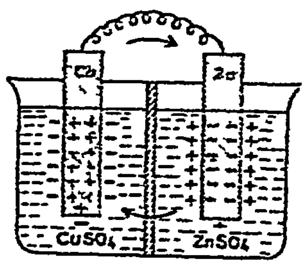


FIG 139 —Daniell's Cell (Diagrammatic)

If a normal solution of copper sulphate be separated by a porous partition, Fig 139, from a normal solution of zinc sulphate, and if a rod of copper be immersed in the copper sulphate be connected by a wire with a rod of zinc immersed in the zinc sulphate (Fig. 139), the zinc pole on the right of the diagram acquires a negative charge on account of the departure of positively charged ions from its surface, and the copper pole on the left acquires a positive charge on account of the departure of negatively charged copper ions from its surface In consequence, an electrical current will flow through the connecting wire from the positively to the negatively charged pole and pass in the converse direction through the liquid. This action continues until all the zinc is dissolved or all the copper precipitated. The relative solution pressures of the two metals decide the magnitude of the resultant electromotive force of the current, and this is the difference of the two effects The resultant electromotive force for the zinc copper couple just described is $+0·493-(-0·606)=0·493+0·606=1·099$ volts. The combination just described represents the so called Daniell's cell (1836) In reality the Daniell's cell contains the zinc rod with the zinc sulphate solution in a porous pot, and the copper plate with the copper sulphate solution in the surrounding jar, as illustrated by the drawing of an uncharged cell in Fig 140 There are many other modifications of Daniell's cell, and numerous other types of cell with different " poles " and different solutions

The *quantity* of electricity produced depends upon the amount of zinc consumed (Faraday's law), and the *rate* at which electricity is developed

—the strength of the current—depends upon the rate at which the zinc is consumed in the cell The *difference of potential* cannot exceed 1 099 volts for the given solutions If the term *ampere* be employed to represent a current equivalent to one coulomb per second, the product of the number of amperes into the number of volts gives the rate of production of electricity or by the cell

EXAMPLE —The electrolysis of 36 5 grams of hydrochloric acid requires 96,540 coulombs of electricity at 1 31 volts Hence the electrical energy needed for this work is 96,540 × 1 31 = 126,567 units, or, defining a joule as the unit of electrical energy consumed per second by a current of one ampere working against a resistance of one ohm (joules = volts × coulombs) the electric energy needed to decompose 36 5 grams of hydrochloric acid is 126,567 joules

Although the difference of potential of a given cell, say a Daniell's cell, is not affected by variations in the size or shape of the poles, or upon the quantity of liquid in the cells, the difference of potential is altered by changing the concentration of the solutions In general, the difference of potential between a metal and a solution of one of its salts is greater with increasing dilution. A tenth normal solution of zinc sulphate, for instance,

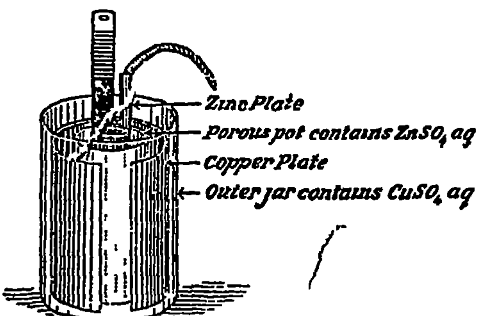


FIG 140 —Daniell's Cell

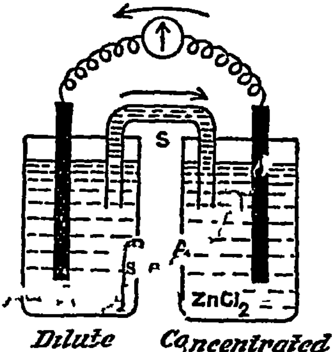


FIG 141 —Concentration Cell.

will give a difference of potential of 0 551 volt, whereas with a normal solution a potential difference of 0 493 volt is obtained as indicated above

If two rods of zinc be separately placed in a solution of zinc sulphate, the difference of potential in both "tends" to drive an electric current from the metal to the solution with a pressure of 0 493 volt If both rods be joined by a wire, no electric current will flow because the two equal forces are oppositely directed On the other hand, if the zinc rods be dipped in solutions of a *different* concentration, the two contact differences of potential will be different, and an electric current will flow from the concentrated solution to the dilute solution outside the cell as indicated in Fig 141 Here a normal solution of zinc chloride is supposed to be placed in one vessel, *A*, and a decinormal solution of zinc chloride in the other vessel *B* Zinc rods connected by a copper wire and galvanometer are dipped into the solutions, as illustrated in the diagram, and the two cells are connected by a syphon tube *S* The difference of potential of the zinc in the normal solution is + 0 493, and in the more dilute solution + 0 551 volt Hence an electric current tends to pass from the metal to the dilute solution with a force of + 0 551 volt, and from the metal to

the concentrated solution with a force of 0 493 The resultant pressure is therefore 0 551 − 0 493 = 0 058 volt, and this represents the electromotive force of the combination Cells in which the electromotive force is generated by the difference potential of two plates immersed in solutions of the same salt at different concentrations are called concentration cells The chemical action which occurs in the two cells tends to bring the two solutions to the same concentration. The action is made clear by the experiment illustrated in Fig 142 A layer of a concentrated solution of stannous chloride, about 10 cm deep, is placed at the bottom of a cylinder, and above this a layer of a dilute solution. A rod of metallic tin is fixed through a hole in the cork so that it is suspended axially in the liquid in the cylinder The rod of tin thus represents both electrodes and connecting wire of a concentration cell Tin is dissolved by the more dilute solution, and precipitated from the more concentrated solution The diagram illustrates the appearance of the rod of tin after the vessel has stood a couple of days.

There is another interesting feature about a concentration cell If an external electromotive force be applied so as to force an electric current to pass in a reverse direction to that which the combination normally furnishes when it is employed as a voltaic cell, the chemical actions will be reversed, and the difference in the concentration of the two solutions will be augmented Such combinations are called reversible cells in contradistinction to irreversible cells in which the original condition cannot be restored by sending a current through the cell in a reverse direction to the current normally delivered by the cell. The cell illustrated in Fig 3 is an irreversible cell, Daniell s cell, Fig 140, and the concentration cell, Fig 141, are reversible cells

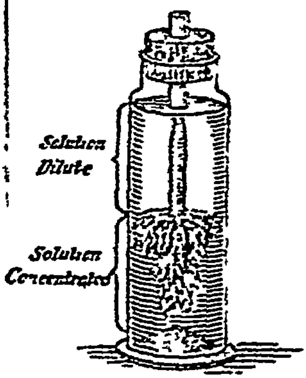
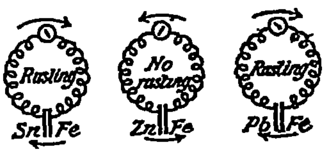


FIG 142 —Experiment on Concentration Cells

Couples —If metallic zinc dissolving in, say, dilute sulphuric acid be in contact with a piece of copper or platinum the rate of dissolution of the zinc is augmented The combination is really a small galvanic cell with zinc, and, say, platinum electrodes connected together by metallic contact Much of the hydrogen is evolved from the surface of the platinum as might be expected from the description of Fig 3 Such a combination is called a *couple*

Sacrificial metals —We have seen that any metal in the electrochemical series can be made one plate of a cell against a metal lower down in the series Zinc for instance, can be made the positive plate against a negative plate of iron, tin, lead, etc , and iron the positive plate against a negative plate of tin, lead etc The further apart the elements in the series, the greater the electromotive force of the combination *Tin-plate* is iron or steel coated with a thin layer of tin If a little moisture be precipitated on the surface in contact with both the iron and the tin, the moisture, with its dissolved carbonic acid, dissolves the iron producing salts of iron, these ultimately form rust (*q v*) The iron is covered with a layer of tin to protect it from rust, but if there be a flaw in the protecting surface of tin so as to expose the underlying iron, rusting takes place more rapidly than if the iron had not been tinned at all The tin remains untarnished Zinc is also used as a protecting layer over the

surface of thin iron plates—*galvanized iron* The voltaic action developed when the protecting layer is damaged is much less than when tin is used. These facts can be illustrated by fitting up a cell like Fig 3 with iron and tin plates, and another cell with iron and zinc plates Water saturated with carbon dioxide is used in both cells A feeble electric current will flow from the tin to the iron outside the cell in one case, and from the iron to the zinc in the other as illustrated graphically in the adjoining diagram.



In the iron tin cell, iron dissolves and rusting occurs, while in the iron zinc cell, the zinc dissolves and no rusting occurs as long as the circuit is closed These results might almost have been predicted from our study of Table XXIII, p 363 An iron lead cell behaves like an iron tin cell Iron railings are often fixed in a bed of lead, the iron corrodes first and the lead remains intact H. Davy (1824) once proposed to prevent the corrosion of the copper sheathing of ships by fixing pieces of metallic zinc here and there on the sheathing The zinc was corroded and the copper preserved.[1] In all these cases it has been fancifully said that one metal is sacrificed to ensure the safety of the other, and all the cases quoted are examples of galvanic couples Fe Sn, Zn Fe, Fe Pb, and Zn Cu

§ 3 The Ionic Hypothesis in Difficulties

The knowledge of nature as it is—not as we imagine it to be—constitutes true science —PARACELSUS

There are some enthusiasts who claim that "all chemical reactions are reactions between ions, molecules as such do not react at all" This statement is not quite in harmony with known facts The same might be said of the assumption that "chemical activity is proportional to the number of available ions" L Kahlenberg (1902 *seq*) has brought forward so large a number of exceptions to these statements that it will be necessary to modify the hypothesis very materially before it can be accepted as an accurate description of the facts Some chemical reactions proceed very rapidly in solutions which are considered to be non conductors of electricity, and which, *ex hypothesi*, are free from ions For instance, dry hydrogen chloride precipitates chlorides from benzene solutions of the oleates of copper, cobalt, and nickel, dry hydrogen sulphide precipitates sulphides from benzene solutions of the same salts and of arsenic chloride All this in spite of the fact that these solutions do not conduct electricity appreciably Again, dry ammonia does not unite with dry hydrogen chloride, but union does take place if a trace of non conducting benzene vapour be present One metal can displace another from a non conducting solution in a non-aqueous medium Thus metallic lead, zinc, tin, silver, iron, etc, will precipitate metallic copper from solutions of various salts in carbon disulphide, carbon tetrachloride, ether, alcohol, etc Hence, in spite of the ionic hypothesis, chemical reactions do take place in non-conducting solutions, and these reactions are similar in result and speed to those which occur in conducting aqueous solutions The ionic hypothesis cannot, therefore, ignore these observations if it is to win a permanent place among the conquests of science

[1] The copper then ceased to poison the barnacles, and the bottom fouled as if the wood had not been sheeted with copper

§ 4. Polarization—Back Electromotive Force.

When the simple cell Zn | H_2SO_4 | Pt, of Fig. 3, is working, hydrogen is evolved, mainly from the surface of the platinum. The chemical action is vigorous at first, but gradually diminishes in intensity, and finally nearly stops altogether. The curve, Fig. 143, shows the electromotive force of such a cell working with a resistance of about ten ohms in the external circuit after different intervals of time. The rapid drop from an initial electromotive force of 1.3 volts to about half a volt in five minutes, is indicated by the rapid descent of the curve. After five minutes, the electromotive force remained fairly constant at about 0.4 volt, that is nearly 66 per cent. below the initial value. The effect is easily illustrated by connecting an electric bell with such a cell. The bell rings loudly at first, but gradually weakens, and finally stops. If the platinum plate be then removed, the surface will be found covered with a layer of bubbles of hydrogen gas, which has remained on the surface of the plate instead of passing away. If the circuit is broken, the bubbles of gas gradually dissipate from the platinum plate, and the cell then resumes its former electromotive force when the circuit is closed. This temporary reduction in the electromotive force of a cell is said to be due to the polarization of the cell. Polarization is developed by modifications of one or both of the plates, or of the solution produced during the working of the cell.

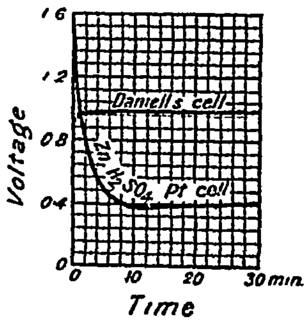


Fig. 143.—Voltage Drop of Voltaic Cells.

In consequence of this phenomenon, commercial cells have some provision for depolarization, that is, for preventing the accumulation of gas on the negative plate. In Daniell's cell, the variation in the electromotive force of the working cell is chiefly due to changes in the concentration of the solution surrounding the battery plates. The electromotive force is therefore nearly constant. This is illustrated by the curve shown in Fig. 143, where a Daniell cell was allowed to work for half an hour against a resistance of 10 ohms in the external circuit. A comparison of this curve with that of the Zn | H_2SO_4 | Pt cell emphasizes the constancy of the current delivered by the Daniell cell.

Again, if a current exceeding two volts be directed through an electrolyte cell (Fig. 5) containing dilute sulphuric acid, and fitted with two platinum plates and a galvanometer in circuit, bubbles of gas are disengaged at the two electrodes, oxygen at the anode, hydrogen at the cathode. The direction of the current is indicated by the deflection of the needle of the galvanometer. Now let the battery be cut out of the circuit, and the electrodes be joined directly with the galvanometer. The deflection of the needle shows that a feeble current passes in an *opposite* direction to that which occurred when the battery was in circuit. An examination of the plates of the polarized electrolytic cell shows that gaseous films are present. Obviously, therefore, after a current has passed through such a cell for a short time, the plates—originally quite similar—are no longer alike. The plates are polarized with different gases. The gases adhere to the surface and penetrate the interior of the plates. The plates

then behave as if they were made of two different materials. Contact differences of potential are established. We have in fact a voltaic cell, O_2 H_2SO_4 H_2, which furnishes a current flowing in an opposite direction to the original current The cell acts as a kind of "accumulator" of electrical energy until the gases absorbed by the plates are used up This does not take long The polarization of the plates of an electrolytic cell thus makes them behave like two different metals which exert a *back electromotive force* opposing the electromotive force of the battery

§ 5 Decomposition Voltages

Suppose a current of ½ volt be sent through the electrolytic cell, Fig 5 containing normal sulphuric acid and fitted with platinum plates in circuit with a galvanometer The current passes through the cell for an instant as indicated by the "throw" of the galvanometer needle, and then the quick drop to nearly zero The hydrogen and oxygen developed on the plates sets up a back electromotive force of nearly ½ volt which very nearly stops the current A minute steady current—residual current—does flow through the system, but this is only just sufficient to maintain the polarization, since if no current at all passes through, the plates would gradually depolarize owing to the dissipation of the gases from the plates

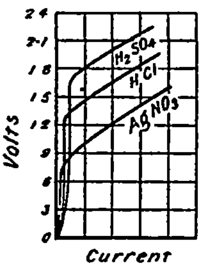


FIG 144 —Effect of an Increasing E M F on some Electrolytes.

If the current be now raised to 1 volt, a similar state of things prevails The amount of oxygen and hydrogen adhering to the plates increases, and the increased polarization raises the back electro motive force to very nearly one volt The residual current passing through the cell is slightly larger than before This is required to maintain the polarization

If the current is now raised to 1 7 volts, the electrodes become saturated with hydrogen and oxygen gases Polarization reaches a maximum value, and the back electromotive force also attains its maximum value Hence any further increase in the applied electromotive force is available for electrolysis, 1 7 volts is the minimum needed for steady electrolysis. If 2 volts are passed through the system, there is a back electromotive force of about 1 7 volts, and the "excess" or "residual" current, 0 3 volt, is the effective electromotive force available for the production of current, and the steady evolution of gases from the electrodes

The facts here described can be exhibited very concisely by plotting the applied electromotive forces as ordinates and quantities of electricity passing through the system as abscissæ Fig 144 shows the results with normal solutions of sulphuric acid, hydrochloric acids, and silver nitrate The "residual" current flowing through the cell with normal sulphuric acid rises very slowly with increasing voltages until the driving force reaches 1 67 volts There is then a sudden change in the direction of the curve Increasing electromotive forces now augment the quantity of electricity passing through the system, and also the amount of electrolysis Normal hydrochloric acid gives a similar break at 1 31 volts, and silver nitrate, one at 0 70 volt

The minimum electromotive force required to cause steady electrolysis

in any solution is called the decomposition voltage or discharge potential The decomposition voltages for a few acids, bases, and salts are shown in Table XXIV

TABLE XXIV —DISCHARGE POTENTIALS OF SOME ELECTROLYTES.

Electrolytes	(Normal solutions)	Decomposition voltages (Volts)
Salts	Zinc sulphate	2 35
	Nickel sulphate	2 09
	Lead nitrate	1 52
	Silver nitrate	0 70
Acids	Sulphuric acid	1 69
	Hydrochloric acid	1 31
	Nitric acid	1 69
	Phosphoric acid	1 70
Bases	Sodium hydroxide	1 69
	Potassium hydroxide	1 67
	Ammonium hydroxide	1 74

While the values for the metallic salts vary from metal to metal, the acids and bases have a decomposition voltage approaching 1 7 volts, and the products of the electrolysis are oxygen and hydrogen. Those acids which have a lower decomposition voltage usually give off other products on electrolysis, and attain the final value—1 7 volts—on further dilution Thus hydrogen and chlorine are evolved when the strength of the hydrochloric acid exceeds $2N$-HCl, and the decomposition voltage of the $2N$ acid is 1 26 volts The voltage steadily rises with increasing dilution until, with $\frac{1}{32}N$-HCl the decomposition voltage is 1 69, and hydrogen and oxygen are the products of electrolysis Not only do the numbers vary with concentration, within certain limits, as exemplified in the case of hydrochloric acid, but also with the nature of the electrodes The decomposition voltage of normal sulphuric acid, for example, with polished platinum electrodes is 1 67 volts, whereas with platinum electrodes covered with platinum black, the decomposition voltage is 1 07 volts

The contact potential between metallic zinc and a *normal* solution of a zinc salt, -0 493 volt, shows that when a zinc ion is deposited on a zinc electrode it conveys a positive charge to the electrode and so lessens the negative charge there present The system is only in equilibrium when the zinc electrode is negatively charged to a potential of -0 493 volt If, therefore, zinc is to be deposited in an electrolytic cell, this difference of potential must be counterbalanced by the current Hence contact differences of potential may also be regarded as decomposition voltages

The discharge potentials of a few anions and cations are indicated in Table XXV, which may be compared with Table XXIV. The numbers refer to normal solutions The prefix refers to the electrical state of the electrode in the presence of a normal solution of its ions, say, 32 5 grams of zinc per litre Some of the numbers have not been measured directly. For instance, the number for zinc sulphate has been obtained

by extrapolation, since, according to the conductivity measurements, only 23 per cent of zinc sulphate is ionized in normal solutions

TABLE XXV—DISCHARGE POTENTIALS OF SOME ANIONS AND CATIONS

Cation.	Charge on metal volts	Anions	Charge in volts
Zn	−0·493	I	+0·797
Fe	−0·063	Br	+1 270
Ni	+0 049	O″ (in acid)	+1 396
Sn	+0 085	Cl′	+1 694
Pb	+0 129	OH′ (in acid)	+1 96
H′	+0·277	OH′ (in bases)	+1 16
Cu	+0·606	NO_3	+1 75
Hg	+1 027	SO_4''	+1 9
Ag	+1 048	HSO_4	+2

Just as different electrical pressures (E M F) are needed to produce in different solutions equivalent amounts of chemical change so different chemical reactions in a voltaic cell generate different amounts of electrical energy, and produce currents with different electromotive forces During electrolysis a difference of electrical pressure must be continuously supplied because the current is consumed, so to speak, by the separation of chemically equivalent quantities of matter (Faraday s law) In a voltaic cell electrical energy is produced, so to speak from the chemical energy of the dissolving zinc The question whether or not a given supply of electrical energy can start electrolysis is determined by the intensity, pressure, or voltage of the current The total supply of available electrical energy does not matter Although a given quantity of electricity, say 96,540 coulombs, will separate chemically equivalent quantities of different electrolytes, these 96,540 coulombs must be supplied at definite pressures before electrolysis can take place In other words, just as different compounds decompose at different temperatures and this quite independent of the total quantity of available heat, so electrical energy at different voltages is needed for the decomposition of different electrolytes

The total amount of electrical energy required for the liberation of chemically equivalent quantities of different electrolytes can be approximately determined by multiplying the 96,540 coulombs (or one farad) of electricity by the voltage needed for electrolysis Hence the decomposition voltage is a measure of the energy needed for the decomposition of a gram equivalent of a given electrolyte A joule, the unit of electrical energy, is numerically equivalent to the product of one volt into one coulomb Further, a joule is equivalent to 0 2382 calories of thermal energy As a first approximation, it may be assumed that the heat of formation of any given compound is a measure of the thermal equivalent of the electrical energy required to break up the compound by electrolysis

EXAMPLE —The heat of formation of sodium chloride is 97,900 calories what is the equivalent electrical energy needed for the electrolysis of a gram equivalent of the fused salt, and what is the decomposition voltage required ? Here, 97,900 calories are equivalent to 97,900 ÷ 0 2382 = 411,000 joules But 96,540 coulombs

will liberate chemically equivalent quantities of sodium and chlorine, and 411 000 joules are needed for this purpose Consequently, since electrical energy = volts × coulombs, 411,000 = volts × 96,540, or volts = 4 3 This means that in order to liberate 23 grams of sodium and 35 5 grams of chlorine from 58 5 grams of fused sodium chloride, 411,000 joules of electrical energy must be supplied at a minimum voltage electromotive force of 4 3 volts The minimum voltages so calculated are usually a little higher than are needed in practice

§ 6 Fractional Electrolysis—Magnus' Rule

When a solution containing salts of different metals is subjected to electrolysis, there is a certain voltage at which one and only one of the metals will be deposited on the cathode—Magnus' rule (1856) If a mixed solution of nickel and copper sulphates, for example be subjected to electrolysis, copper alone is precipitated when the applied electromotive force has reached 1 29 volts, the nickel is not precipitated, since its decomposition voltage is 1 95 volts On the other hand, if a mixture of nickel and iron sulphates be similarly treated, a mixture of iron and nickel will be simultaneously deposited The decomposition voltages of these salts are too close to allow an effective separation of the two elements by electrolysis Hydrogen is also evolved during the electrolysis of these salts This arises from the fact that the decomposition voltage of sulphuric acid —1 67 volts—renders it also susceptible to the influence of the same current as liberates nickel and iron

Many useful methods of analysis are based upon these principles In metallurgy too, electrolytic processes for refining metals—nickel, copper, lead, tin, silver, gold, etc —have been developed For example, in copper refining, as we shall soon see, anodes made of crude copper are dipped in a solution of copper sulphate acidified with sulphuric acid, the cathodes are sheets of pure copper Zinc, iron, and copper from the anode pass into solution during electrolysis The decomposition voltage is kept below that needed for the deposition of zinc and iron In consequence, refined copper is deposited on the cathode Other impurities affecting the crude copper are but slightly soluble in the electrolyte, and are deposited about the anode as a thin mud—"anode mud"

The decomposition voltage of an electrolyte is greater the more dilute the solution The concentration of any given salt about the electrode naturally decreases during the process of electrolysis Hence also the decomposition voltage for that particular salt in the mixed electrolyte also increases When the concentration of the copper sulphate in a mixture of copper and nickel sulphates has become so small that the decomposition voltage of the dilute solution approaches that of nickel, any further electrolysis will bring down a mixture of both metals There is, therefore, a limit to the process of electrolytic separation, just as there is a limit to the separation of substances in ordinary analysis The limit in the former case is determined by the decomposition voltages of the respective metals, and in the latter case, the limit is determined by the solubility of the precipitates in the given menstruum. The limiting concentration can be approximately determined from the rule A decrease of $\frac{1}{10}$ in the concentration of the electrolyte raises the decomposition voltage of any given ion 0 058/m volt, where m is the valency of the particular ion

As the cation is deposited about the cathode, the loss in concentration is made up by diffusion from the surrounding electrolyte To hasten diffusion, and prevent the undue attenuation of the electrolyte in the vicinity of the cathode, stirring by rotating one of the electrodes is sometimes used

If the cathode be small in comparison with the anode, the solution about the former will be very much more quickly exhausted than if a larger cathode had been used The decomposition voltage of the substance will rise in a proportional manner Hence the larger the cathode the lower the "average" electromotive force needed for the deposition of the pure metal It is convenient to call the quantity of electricity flowing through unit surface area, the current density at the electrode, in other words, "the number of amperes per unit surface" "Unit surface" is usually taken in the laboratory to be one square decimetre

EXAMPLE —What was the current density at the anode of the electrolytic cell when 4 sq cm of each electrode were immersed in the electrolyte and a current of 4 25 amperes was passed through the system for one hour? One square decimetre = 100 sq cm Hence, 1 0625 amps passed per sq cm, or 106 25 amps per sq decimetre The current density at the anode was therefore 106 25 amps

Current density is one of the most important factors in electrolysis, since it determines the character and nature of the products obtained at the different electrodes Thus, by using a large current density and a concentrated solution of sulphuric acid, hydrogen, oxygen, ozone, and free sulphur can be obtained, whereas under ordinary laboratory conditions the latter substance does not appear

§ 7 The Factors of Energy

The idea developed in the preceding sections, that electrical energy is dependent upon two distinct factors, may now be extended further Water will only flow from one vessel to another when there is a difference in the level of the liquid in the two vessels The actual volume of the water in either vessel does not matter Again, heat will only pass from one body to another when the temperature of the one is higher than the temperature of the other The flow of heat is not determined by the quantity of heat in either the hot or the cold body If two reservoirs of gas be connected by a cylinder fitted with a sliding piston, the motion of the piston will not be determined by the volume of the reservoir, nor by the quantity of energy contained in the gas, but it will be determined by difference in the pressure of the gas in the two cylinders In this sense we can imagine the different forms of energy to be compounded of two factors —mass of water and difference of level, thermal capacity and temperature, volume and pressure of gas The one factor is called the quantity or capacity factor, and the other the intensity factor or strength

Available energy = capacity (quantity) factor × intensity (strength) factor

When the capacity factor is constant, or nearly so, more work can be got from a definite amount of energy with a high than with a low intensity factor, and a moment's reflection will show that in every transformation the intensity factor will be diminished Energy becomes less available for doing work when the intensity factor is diminished

What are the factors of chemical energy?—If chemical energy can be resolved into two factors, the one factor must be analogous to the capacity, and the other to the intensity factor of thermal energy. J. W. Gibbs calls the intensity factor of chemical energy the chemical potential, and G. Helm calls it the chemical intensity. These terms are employed with the idea of avoiding the vagueness of the old term, chemical affinity, which is undoubtedly the correct designation for "chemical intensity." Now, the quantity of a substance which takes part in any chemical change is proportional to the "equivalent weights" of the substance; and assuming that the chemical equivalent is the capacity factor of chemical energy, we may write—

Chemical energy = equivalent weight × chemical affinity;

or

Chemical energy = equivalent weight × chemical intensity.

If two bodies at the same temperature be placed in contact, there will be no apparent conduction of heat from the one to the other; but when the temperature of the one body is higher than that of the other, heat will pass from the hot to the cold body, so that the cold body is warmed and the hot body is cooled. So with chemical energy. We assume that the molecules of every substance possess a specific amount of chemical energy, which has a definite intensity under certain specified conditions. One substance can only react with another when the intensity of the energy associated with the original mixture is greater than that of the final system. If the intensity of the energy associated with the original mixture be the same as that associated with the products of the reaction no reaction will take place; if the intensity factors are not equal, the energy will not usually be at rest. Water placed in a series of vessels in communication with one another will only come to rest when the surface of the water is at the same level in each vessel. "Difference of level" here means that the gravitational energy has a different intensity factor in each vessel. An electric current will flow whenever there is an inequality of the intensity factor—i.e. a difference of potential—at different parts of the circuit. If the intensity factors of any particular form of energy in a system are not equal, the system will be in a state of unstable equilibrium. Such a condition will not be permanent, and energy will flow, so to speak, from one part to another until the different intensity factors become equal.

Ostwald has drawn attention to the fact that if the chemical process be performed in a voltaic cell, the work derived from that process will be transformed into an equivalent amount of electrical energy. And since, by Faraday's law, the capacity factor—quantity of electricity—is proportional to the quantity of matter decomposed, the capacity factor of the electrical energy will be proportional to the capacity factor of the chemical energy. Hence the respective intensity factors of chemical and electrical energies will also be proportional. But electromotive force is proportional to the intensity factor of electrical energy, and therefore electromotive force is proportional to chemical affinity. We see, then, with Faraday, that "the forces called electricity and chemical affinity are one and the same." Our problem is solved for conductors of electricity—electrolytes. Chemical action takes place when the potential of the reacting substances is greater than that of the reacting products. We can

to day express the "affinity" between a number of reacting substances roughly in terms of difference of potential. How this may be done for non conductors of electricity has not yet been determined.

The temperature or intensity factor of heat energy required for the decomposition of many substances—say calcium or potassium chloride—is so great that commercial methods of decomposing these substances by thermal energy are not profitable. A great many compounds thus appear to be very stable when heated to high temperatures, these can often be decomposed by electrical energy at a comparatively low voltage (intensity factor). This illustrates how the commercial production of metals like aluminium, calcium, etc, were not particularly successful until electrical methods were adopted. The prediction of C. L. Berthollet, 1803, has been fulfilled. "The electric current," said he, "has furnished chemistry with an agent whose energy may be carried to a degree which, as yet, can scarcely be imagined, and which will furnish the means of producing in the formation and decomposition of chemical combinations, effects unforeseen, and superior to those which it is possible to obtain by the action of heat." It has been suggested, too, that if a source of energy with a particularly high intensity factor were available, it would most likely be possible to decompose many of the so-called elements into still simpler substances, but this, of course, is merely a speculation.

Questions

1 What is the weight in grams of (a) iron, (b) aluminium which would theoretically be required to remove (i e precipitate) the copper completely from a solution containing one kilogram of crystalline copper sulphate, $CuSO_4 \cdot 5H_2O$ (Cu = 63 5, Zn = 65, Al = 27, O = 16, S = 32, H = 1)?—*Sydney Univ*

2 How much silver will be deposited from a solution of silver nitrate by a current of 2 amperes in 30 minutes?

3 Explain the meanings of the terms "electropositive" and "electronegative" as applied to the elements.—*London Univ*

4 What weight of silver and copper would be deposited by an electric current flowing through a solution of those metals in the same time that it liberates 30 c c (at n.p t) of a mixture of oxygen and hydrogen from acidulated water (Cu = 63, Ag = 108)?—*London Univ*

5 The solution pressures of the five elements manganese, zinc, tin, hydrogen, copper, and oxygen decrease in the order in which they are named. What might be expected to occur (and why) when (a) metallic manganese is placed in a solution of copper, (b) when metallic copper is placed in a solution of a tin salt, (c) when metallic manganese is treated with an acid, (d) when tin is treated with a weak acid, and (e) when copper is treated with an acid?—*Massachusetts Inst Technology*

6 Show how the evolution of hydrogen when metallic iron is treated with hydrochloric acid is comparable with the deposition of lead upon a strip of zinc when the latter is immersed in a solution of a lead salt.—*Massachusetts Inst Technology*

CHAPTER XXI

COPPER, SILVER, AND GOLD

§ 1 Copper—Occurrence and Properties

History—Copper appears to have been known from prehistoric times—the neolithic age The "copper age" followed the "stone age" Copper appears to have been used for making utensils and instruments for war before iron This is probably due to the fact that copper occurs native in a form requiring no metallurgical treatment The ancients used the terms χαλκός (chalcos) and *aes* for copper, brass, and bronze Copper was afterwards called *aes cyprium* (*i e* Cyprian brass), since the Romans first obtained it from the Isle of Cyprus, the term *aes cyprium* was soon abbreviated to *cuprum* Hence the modern symbol "Cu" The seven metals—gold, silver, mercury, copper, tin, iron, and lead—known to the earlier chemists were designated by the names and symbols of the seven greater heavenly bodies—Sun, Moon, Mercury, Venus, Jupiter, Mars, and Saturn Thus the looking-glass of Venus ♀ symbolized copper. In some cases it is possible to see a reason why a particular metal was assigned to a particular heavenly body, but in other cases the connection is more remote

Occurrence—Metallic copper is found in many localities, *e g* considerable masses have been found in Michigan on the shores of Lake Superior, and small quantities in many other places—Cornwall, Siberia, Ural, Australia, Chili, etc Compounds of copper are distributed in nature as oxide in *cuprite*, or ruby ore, Cu_2O, as sulphide in *chalcocite*, or copper glance, Cu_2S, copper pyrites or *chalcopyrite*, $CuFeS_2$ or Cu_2S Fe_2S_3 The real composition of many copper sulphides, as they occur in nature, is exceedingly complex The same remark is more or less true for the composition of most natural minerals, at least chemical formulæ which follow the analyses closely are very complex The formulæ for minerals are commonly represented as if pure minerals occurred in nature Ideally pure minerals very seldom occur in nature, and accordingly, the formulæ represent ideal or imaginary minerals to which real minerals approximate more or less closely Copper also occurs in many places as basic carbonate, *malachite*, $CuCO_3$ $Cu(OH)_2$, and *azurite*, $2CuCO_3$ $Cu(OH)_2$ Copper silicates, arsenates, phosphates, etc, are also known to occur native Copper has also been found in the feathers of some birds

Properties—Copper has a characteristic reddish-brown colour by reflected light, but in transmitted light, thin layers are green The metal can be obtained in octahedral crystals (cubic system) When near its melting-point, copper is brittle enough to be powdered If a piece of copper be heated and cooled slowly, it is brittle, and if cooled rapidly, it

is soft, malleable, and ductile Copper is one of the best conductors of heat and electricity These properties are modified if the metal be contaminated with minute traces of impurity Copper melts at 1082 6° in an atmosphere of carbon monoxide, and it can be distilled in the electric furnace It furnishes a green vapour, and it colours Bunsen's flame green Dry air has no action on copper, but in the presence of atmospheric moisture and carbon dioxide, the metal becomes covered with a green basic carbonate called "verdigris" The atmosphere of towns containing sulphur oxides may also form basic sulphates with the copper Hydrochloric and sulphuric acids have little or no action on the metal in the cold, hot sulphuric acid dissolves copper rapidly, and hot hydrochloric acid attacks the metal slowly Nitric acid—hot or cold, dilute or concentrated—dissolves the metal rapidly, forming copper nitrate Ammonia acts on copper in the presence of air forming a deep blue solution

Atomic weight.—The combining weight of copper has been determined by the analysis or synthesis of the oxide, sulphate, chloride, etc The results, referred to oxygen = 16, vary between 63 35 and 63 68, and the best representative value is taken to be 63 57 This number also represents the atomic weight, as estimated by the isomorphism of the cuprous, silver, and gold salts, by the vapour density of the volatile copper compounds, and by Dulong and Petit's method of approximation—specific heat of copper 0 0956

Uses.—Next to iron, copper is the most useful metal Enormous quantities are used in the electrical industries It is also made into household utensils, boilers, etc Copper nails, rivets, and sheeting are used for sheathing ships because copper is but slowly corroded in moist air and in sea water Copper is one of the chief ingredients in small coins. *British copper coins* contain 95 per cent of copper, 4 per cent of tin, and 1 per cent of zinc Gold and silver coins of different nations usually contain 8–10 per cent of copper *Nickel coins* in Germany and the United States contain about 25 per cent nickel, and 75 per cent of copper Copper is largely used in the manufacture of alloys With zinc it forms *brass* (zinc 1, copper 2–5)—*common brass* has zinc 1, copper 2, *Dutch metal* (zinc 1, copper 4), *bell metal* (copper 3, zinc 1), with tin, *speculum metal* (tin 1, copper 2) used for optical instruments, *gun metal* (tin 1, copper 9) was once used for making cannon *Bronze* is an alloy of copper (70–90 per cent), zinc (1–25 per cent), and tin (1–18 per cent), it is used for making statues, coins, ornaments, etc *Phosphor bronze* contains tin and a small percentage of phosphorus, *manganese bronze* employed for propeller blades has about 0 3 per cent of manganese The manganese alloys are tougher than ordinary bronze, and they are largely used for steamship propellers because they resist corrosion by sea water fairly well, and certain parts of machinery *Aluminium bronze* contains 95 per cent. of copper, it is a hard yellowish brown alloy, light, strong, and elastic It is used for making the hulls of yachts, etc *German silver* contains copper (56–60 per cent), zinc (20 per cent), and nickel (20–25 per cent) It is used in making resistance coils (owing to its low electric conductivity), and for imitating silver

§ 2 Copper—Extraction.

The methods employed for winning copper from its ores depend upon the kind of ore used, and upon local conditions Similar ores

are seldom treated in the same manner in different localities. If the ore contains no sulphur—as is the case with the carbonates and oxides—the metal can be obtained by simply reducing the ore with coke in a furnace heated by a blast. Assuming that the ore to be smelted is a typical chalcopyrite, the operations involved in extracting the copper are somewhat complex because (1) a large number of impurities are present in the ore, (2) copper of a high degree of purity is needed, and (3) it will probably be profitable to recover gold and silver from the crude metal.

1. **Roasting the ore.**—The pyritic ore is first crushed, and it may or may not be necessary to concentrate the pyrites by washing away the rocky impurities. The concentrated ore, in one works, contained about 14 per cent. of copper, and 29 per cent. of iron. Part of the concentrated ore is then roasted, say, in a reverberatory furnace in order to convert the sulphides into oxides: $2CuFeS_2 + 6O_2 = Cu_2O + Fe_2O_3 + 4SO_2$. It may or may not be convenient to use the sulphur dioxide for the manufacture of sulphuric acid.

2. **Fusion for matte.**—A mixture of roasted and unroasted ("green") ore and coke is charged into a blast furnace lined with firebricks and heated by a blast. The air blast burns the carbon to carbon monoxide: $2C + O_2 = 2CO$. Part of the cuprous oxide formed in the preceding operation is reduced to copper by the joint effect of the carbon and carbon monoxide: $Cu_2O + CO = 2Cu + CO_2$. The copper unites with the sulphur of the unroasted ore: $3Cu + Fe_2S_3 = 3CuS + 2Fe$; and some of the unreduced cuprous oxide forms cuprous sulphide: $3Cu_2O + Fe_2S_3 = 3Cu_2S + Fe_2O_3$. Any cupric sulphide present is reduced to cuprous sulphide. The ore probably contains silica, if not, some must be added when the furnace is charged. Part of the iron unites with the silica to form a fusible slag, and part is reduced to ferrous sulphide which remains admixed with the cuprous sulphide to form matte. Matte is a more or less impure mixture of cuprous and ferrous sulphides containing 45–75 per cent. of copper. The gold and silver, and part of the arsenic and antimony in the ore remain with the matte. The furnace is then tapped, and the matte and slag are run into a trough. The lighter slag rises to the surface and flows over into a pit. The matte, which collects at the bottom of the trough, is drawn off from time to time.

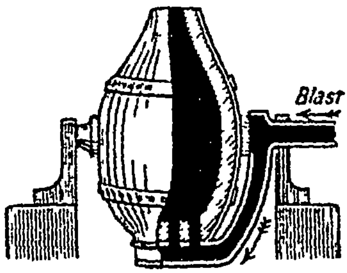


FIG. 145.—"Converter" Furnace (Diagrammatic).

3. **The conversion of the matte into blister copper.**—The molten matte is run into a tilting "converter" furnace lined with a mixture of quartz and clay, and arranged with openings in the bottom so that air can be blown through the molten matte, Fig. 145. The sulphur, iron, and many other metals are oxidized. The volatile oxides are driven off, the iron oxide unites with the siliceous lining of the converter to form a slag. The iron and sulphur are oxidized first. As soon as appreciable quantities of copper commence to oxidize, the operator can tell from the appearance of the flame issuing from the converter that it is time to stop the blast. The furnace is then tilted, and the copper is run off. As the copper cools, the sulphur dioxide dissolved by the metal is expelled, this gives

the metal a blistered appearance, hence the product is called blister copper

4 The conversion of blister into crude copper —The blistered copper is melted on the hearth of a reverberatory furnace—*e g* Fig 174—and any oxide dissolved by the copper is reduced by forcing a log of green wood into the molten mass The hydrocarbons of the wood, bubbling through the molten metal, reduce copper oxide to metallic copper The "poled" copper is cast into plates—about ⅜ inch thick, 3 feet wide, and 3 feet long —if it is to be further purified

5 Refining the crude copper by electrolysis —Crude copper is refined by an electrolytic process Plates of crude copper are suspended, as anodes, in a bath of copper sulphate acidified with sulphuric acid Sheets of pure copper, as cathodes, are suspended alternately with the anodes in the same bath When the current passes, copper dissolves from the anodes, and pure copper is deposited at the cathodes. The impurities in the crude copper either pass into solution, or are deposited as a mud or "slime" about the anode The anode is enclosed in filter cloth bags to facilitate the collection of the "anode mud" Considerable amounts of silver and gold are obtained from the slimes or "anode mud" It is possible to get a very high degree of purity—*e g* 99 8 per cent copper—by the electrolytic process This quality of copper is needed for electrical purposes, since a trace of impurity may considerably reduce the electrical conductivity of the metal Copper matte, blister copper, and even copper ores have been treated, more or less successfully, by electrical processes, but the product is not very pure

§ 3 Silver—Occurrence and Properties

History —Silver has been known from ancient times There are some allusions to silver in the Old Testament, and it was probably used as money as early as gold The Phœnicians are supposed to have obtained their silver from Armenia and Spain Silver appears to have been purified by a process of cupellation, but there is little evidence to show that the ancients knew how to separate silver from gold The old terms for silver refer to its bright white colour—the Hebrew equivalent is derived from the verb "to be white," and the Greek term from ἀργός (argos) to be shining The early chemists termed silver "Luna," or "Diana," and represented it by the symbol ☽ for the crescent moon—probably because of the pale silvery colour of moonlight

Occurrence —Native silver is occasionally found in large masses or crystallized in cubes or octahedra It is also found associated with metallic copper, gold, etc The principal ores of silver contain silver glance or *argentite*, Ag_2S, admixed with several other sulphides—antimony, arsenic, and copper The chief silver ores are found in Mexico, Peru, Chili, Bolivia, Idaho, Arizona, Norway, Australia, etc Much silver also occurs associated with lead in galena, and a great deal of the silver in commerce is extracted from argentiferous lead Silver chloride, AgCl, occurs as *kerargyrite*, or horn silver

Properties of silver —Silver is a white lustrous metal which appears yellow if the light be reflected from its surface many times before it reaches the eye Very thin layers of silver have a bluish tint Powdered silver

is grey and earthy in appearance Silver is highly malleable and ductile. Sheets 0·00001 inch thick have been made Silver melts at 960° in an atmosphere of carbon monoxide and vaporizes between 1200° and 1500°. It can be distilled in the oxy-hydrogen blowpipe or in the electric furnace. The vapour appears of a greenish colour Molten silver absorbs oxygen as indicated when the occlusion of gases by the metals was under consideration. Silver conducts heat and electricity better than copper Exposure to the air has no action on silver, but if the air be contaminated with hydrogen sulphide, the silver is blackened owing to the formation of a thin film of silver sulphide on the surface (Nitric acid—hot or cold, dilute or concentrated—readily dissolves the metal. forming silver nitrate Hot concentrated sulphuric acid gives silver sulphate, but the metal is not perceptibly attacked by dilute acid. Hydrochloric acid acts very slowly, if at all, at ordinary temperatures, but at a red heat, hydrogen chloride forms silver chloride)

Atomic weight.—Analyses of various halogen compounds of silver give numbers ranging from 107 67 to 108·09 for the combining weight of silver (oxygen = 16), the best representative value is supposed to be 107 88 which also represents the atomic weight This number agrees with the isomorphism of the silver, gold copper, and sodium salts, and also with Dulong and Petit s method of approximation—specific heat of silver, 0 05625

Uses —British silver coinage has very nearly 92 5 per cent of silver and 7 5 per cent of copper This is the standard of *sterling silver* for coinage and for silver plate regulated by law The American dollar has about 90 per cent of silver Silver ornaments made from standard silver can be heated in air to oxidize the copper near the surface of the metal, the resulting copper oxide is removed by digestion with sulphuric acid, leaving a superficial layer of pure silver The effect so produced is called "frosted silver" The so-called "oxidized silver" is made by dipping silver ornaments in a solution of an alkaline sulphide A thin film of sulphide is thus formed on the surface.

§ 4 Silver—Extraction

The methods employed for the extraction of silver are varied.

1. Lixiviation processes —In Ziervogel's process, the ores are roasted under carefully regulated conditions so that the iron and part of the copper sulphides are converted into oxides, while the silver and part of the copper are converted into silver and copper sulphates Ag_2SO_4, $CuSO_4$ The soluble sulphates are extracted with water, and the silver precipitated from the solution by the addition of scrap copper The copper is afterwards precipitated by the addition of iron This process was once much used for argentiferous copper mattes In Percy and Patera's process the ore is roasted with salt; silver chloride is formed. This is extracted with sodium thiosulphate; or with strong brine, as in Augustin's process In Percy and Patera's process the silver is precipitated from the solution as silver sulphide by the addition of sodium or calcium sulphide and reduced to the metal by calcination in a roasting furnace, in Augustin s process, the silver is precipitated by scrap copper. The modern cyanide process has practically ousted the lixiviation processes just indicated.

In the cyanide process, the crushed ore is treated with a solution of potassium or sodium cyanide The cyanide reacts with the silver sulphide $Ag_2S + 4NaCy \rightleftharpoons 2NaAgCy_2 + Na_2S$ The accumulation of sodium sulphide in the solution stops the reaction When the solution is exposed to the air, however, the sodium sulphide is oxidized to sodium thiosulphate and sulphur The reaction then progresses as indicated in the equation from left to right Thus, the free access of air to the cyanide solution is an important factor in promoting the dissolution of silver The silver is recovered from the solution by zinc precipitation

2 Amalgamation processes —In Mexico, where fuel is scarce, the so called patio process has been in use over 300 years, but now it is almost displaced by the cyanide process Hence the patio process promises very soon to be of little more than historic interest In this process, the powdered ore is thoroughly incorporated with a little sodium chloride In about a day, mercury is added along with some roasted pyrites containing a mixture of copper and iron sulphates and oxides The whole is most intimately mixed, and more mercury added from time to time It is probable that copper chlorides are first formed, and these decompose the silver sulphide $CuCl_2 + Ag_2S = 2AgCl + CuS$, and $2CuCl + Ag_2S = 2AgCl + Cu_2S$ The silver chloride dissolves in the brine, and it is then immediately reduced by the mercury $AgCl + Hg = HgCl + Ag$ The mercury is more active if about 1 per cent of sodium be dissolved in it The resulting silver amalgam is separated from the mud by washing and settling, and the excess of mercury is squeezed through canvas bags The solid amalgam is then pressed into cakes, and heated in a retort. Mercury distils over, and silver remains behind A certain amount of mercurous chloride is lost during the operations

3 Smelting process is largely used in America The object is to concentrate the silver in lead The ore is mixed with coke and limestone, and heated in a small blast furnace A fusible silicate of iron and lime is formed as a slag, and the reduced metal accumulates in the bottom of the furnace Slag and metal are run off from time to time The "pigs" of lead are passed on for desilverization

4 Electrolytic processes —The electrolytic process indicated in our study of copper extraction is used for the separation of silver from argentiferous copper In B Moebius' process (1884), the electrolyte is a mixture of silver and copper nitrates acidified with nitric acid A slab of impure silver is used as anode, and a plate of pure silver as cathode Silver and copper are dissolved at the anodes, and silver is precipitated on the cathodes. The gold, if present, remains undissolved as a slime below the anode The anodes are enclosed in filter bags to facilitate the collection of the "anode mud" The composition and concentration of the solution, as well as the current density are carefully regulated on account of the danger of depositing copper with the silver

§ 5 Desilverization of Lead

Lead can be desilverized by means of Pattinson's or Parkes' process The latter process is generally used, the former but seldom

I Pattinson's process —Molten lead and silver mix together in all proportions. The melting points of all possible alloys of the two metals

are indicated in Fig 146 There is a eutectic at 303°, when the molten mixture contains $2\frac{1}{2}$ per cent of silver If a molten mixture of lead with, say, 50 per cent of silver be allowed to cool, when the temperature reaches 648°, some silver (contaminated with a little lead) will separate from the solution The remaining fluid is richer in lead than it was before, and consequently remains fluid, but as its temperature falls, more silver will separate from the solution and the mother liquid will continually get poorer and poorer in silver until but $2\frac{1}{2}$ per cent remains. The whole will then freeze *en masse* at 303° If the molten mass contains less than $2\frac{1}{2}$ per cent of silver, it will begin to freeze somewhere between 327° and 303°, and lead (contaminated with a little silver) will separate from the solution, and continue separating until the mother liquid has $2\frac{1}{2}$ per cent of silver when all will freeze *en bloc* The results are here quite analogous with the freezing of solutions of salt and water indicated in an earlier chapter In Pattinson's process for separating silver from lead, the molten mixture containing less than $2\frac{1}{2}$ per cent of silver is allowed to cool slowly, and the crystals which separate from the cooling solution, containing more lead than the original solution, are skimmed off with perforated ladles into a neighbouring pot until one-third to one eighth of the original solution remains. The enriched silver-lead alloy remains in the pot The operations are repeated on both fractions until the enriched lead contains about one per cent of silver, and the desilverized lead contains but 0 001–0 002 per cent of silver The theoretical enriched lead should have $2\frac{1}{2}$ per cent of silver The enriched lead is then cupelled for silver—see "Gold refining by cupellation"

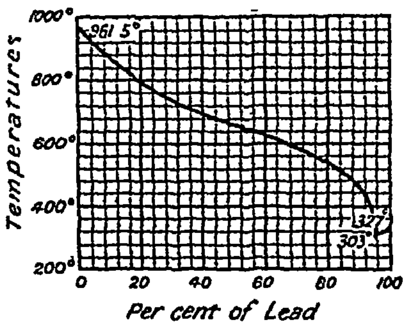


FIG 146—Freezing Curve of Silver : Lead Alloys

II Parkes' process —Zinc readily forms a number of chemical compounds with silver—Ag_3Zn_2, $AgZn$, Ag_2Zn_3, Ag_2Zn_5, $AgZn_{12}$ They all show maximum points on the freezing point curve of alloys of zinc and silver These compounds all freeze at a higher temperature than molten lead, and they are specifically lighter than molten lead Hence if molten zinc be stirred in a bath of molten argentiferous lead, and the molten mixture be allowed to cool, a crust is formed on the surface containing a zinc-silver compound Gold in the argentiferous lead also passes with the silver to the zinc The zinc silver crystals are removed from the surface as they are formed until the lead itself begins to solidify The process can be repeated until finally the remaining lead contains but 0 0005 per cent of silver The desilverization can thus be carried much further by this process than is practicable with Pattinson's In practice, the zinc added to the lead is kept between 0 8 and 1 5 per cent, and the zinc-silver crystals are mainly Ag_2Zn_5 The mixture of zinc, lead, etc., is heated on an inclined surface hot enough to melt the lead, but not the zinc alloy The lead flows away, and the enriched scum remains The zinc can be separated from the silver, gold, and lead, by distillation. The residue in the retort containing the silver and gold is cupelled.

§ 6 Gold—Occurrence and Properties

History.—Gold must have been one of the earliest of metals to attract the attention of primitive man. Flint daggers with gilt handles have been reported from excavations in Egypt, and gold is mentioned in the earliest writings of civilized man. The gold mines of Nubia were worked extensively by the Egyptians. Pliny described the amalgamation process for the extraction of gold. Cupellation processes for the purification of gold were described in the second century, and the same process is probably referred to by Jeremiah in the Old Testament, 600 B.C. The earliest words for gold in Hebrew and Egypt refer to its shining appearance. The early alchemists called gold *sol* (the sun) and represented it by the symbol of perfection ○ or ☼, not on account of its appearance, but because they considered it to be the most perfect of the noble metals—the very king of metals.

Occurrence.—Gold is generally found in a metallic condition in quartz veins, and in alluvial gravels—the latter represent the *débris* from the weathering of auriferous rocks. Native gold is never found pure, but specimens 99 per cent. purity are sometimes found; and one from Cripple Creek (Colorado) was reported to be of 99.9 per cent. purity.

Metallic gold is very widely distributed in nature in quantities *too small* to be profitably extracted. Sea-water, for instance, is said to contain about 3½ grains per ton. Granite, on the average, has about 0.37 part per million; sandstones, 0.03 part per million; limestones, 0.007 part per million. Gold also occurs in small quantities in clays, iron pyrites, and in almost all silver, copper, bismuth, lead, zinc, tellurium, and antimony ores. Gravels which need not be crushed can sometimes be profitably treated for gold—alluvial gold—if about 2 to 3 grains per ton be present, that is, one part of gold per 5 million parts of worthless material. The mean of the returns for the Rand is something less than half an ounce of gold per ton of material treated.

Properties.—Gold in mass is yellow, but it appears red if the light be reflected many times from the surface of the metal before it reaches the eye. Gold leaf is green or blue in transmitted light; and if precipitated in a fine state of subdivision the tint varies from red to dark brown. Very thin films of gold are crimson or purple in transmitted light. Gold crystallizes in the cubic system. It is one of the most malleable and ductile of metals, sheets 0.0000004 inch thick have been made. It is not quite so good a conductor of heat and electricity as silver and copper. Gold melts at 1062.4°, and the molten metal appears green. It begins to volatilize at temperatures just above its boiling point. Krafft and Bergfeld say that the metal boils at 2530°. Gold occludes oxygen, hydrogen, and carbon monoxide under suitable conditions. Gold is not acted upon by air or oxygen at any temperature, hence the alchemists called gold a *noble metal* in contrast with *base metals*—like copper, lead, tin, etc.—which are oxidized and lose their metallic character when heated in air. Silver and platinum are noble metals for the same reason as gold. The inert gases argon and its congeners have been called *noble gases* because they are chemically inactive.

Solvents for gold.—Gold is scarcely affected by nitric, sulphuric, and hydrochloric acids, but it is dissolved by aqua regia; by water

containing the halogens chlorine, bromine, or iodine in solution, and by solutions which can generate the halogens Gold is attacked by boiling ferric chloride solutions, hot selenic acid, telluric acid with sulphuric or phosphoric acid, alkaline sulphides and thiosulphates, perchlorates, perbromides, and periodides of the metals, iodic and periodic acids with hot sulphuric acids, and by reacting substances which give large quantities of oxygen—manganese dioxide or potassium permanganate or nitric acid with sulphuric acid—and aqueous solutions of potassium cyanide when exposed to the air. Gold is not appreciably attacked by solutions of the alkalies The freezing point of a solution of gold in mercury corresponds with a monatomic molecule Au

Atomic weight —Analyses of gold chloride, gold bromide, and some of the aurates furnish values for the combining weight between 197·05 and 198 25; the best representative value appears to be 197 2 This number probably represents the atomic weight judging from the isomorphism of the silver, cuprous, aurous and sodium salts, and from Dulong and Petit s method of approximation—specific heat of gold, 0 0316

Uses —British gold coinage contains 91 66 per cent of gold and 8 33 per cent of copper This is called *sterling or standard gold* The gold coinage of Sydney mint has the same amount of gold, but silver is used in place of copper, so that the Sydney sovereign is greenish-yellow The amount of gold in alloys is usually expressed in terms of the *carat* Here, 1000 parts are divided into 24 equal parts. Pure gold is 24-carat gold The sovereign is a 22-carat alloy because it contains 22 parts of gold per 2 parts of other metals. The standard gold alloys recognized by law are 22-, 18-, 15-, 12-, and 9-carat or parts of gold per 24 parts of alloy Ware made by these standard alloys can be "hall-marked" American gold coinage has 90 per cent of gold and 10 per cent of copper

§ 7 Gold—Extraction and Refining

Washing processes —The amount of gold in a ton of ore is small, and in consequence relatively large quantities of ore have to be treated. Gold is separated from alluvial gravel by mechanical washing The specific gravity of gold is so much greater than that of the associated materials, that, when the mixture of sand and gravel is agitated with water in large pans or "cradles," and the rocky matters floated off, the fine particles of gold remain on the bottoms of the cradles as "gold dust" This primitive method of washing has been replaced by placer mining, in which the sand containing the gold is agitated in sluices, that is in long flumes or troughs with transverse cleets along the bottom, and through which powerful streams of water flow The water sweeps away the sand, and the heavier gold collects on the bottom of the sluices In hydraulic mining, water under high pressure is directed against the "earth" containing the gold The "earth" and gold are washed into the sluices as in placer mining In vein mining, the gold-bearing quartz is mined by blasting, etc ; the quartz is crushed to fine powder in stamper mills, and the gold extracted by one of the following processes

Amalgamation process —The powder from the stamper mills is floated as a "slime" in a large trough through which water is continually flowing The slime then runs over copper plates amalgamated with mercury The

particles of gold amalgamate with the mercury After some time the plates are scraped, and the mercury removed from the scrapings by distillation Gold remains behind in the retorts The "tailings" which have passed over the copper plates can usually be profitably treated by the cyanide process, and more gold extracted

Chlorination process—Gold can be extracted from pyrites by the chlorination process The ore is first roasted, then wetted, and exposed in revolving barrels to the action of chlorine gas The gold forms auric chloride, $AuCl_3$, which is extracted by water, and precipitated from the solution by ferrous sulphate, or by hydrogen sulphide—followed by roasting of the precipitated sulphide

Cyanide process—The powdered ore is leached with a dilute aqueous solution of potassium cyanide (0 25 to 1 per cent) while freely exposed to the atmospheric air Under these conditions, gold is dissolved as a double cyanide $4Au + 8KCy + 2H_2O + O_2 = 4KOH + 4KAuCy_2$ Gold is precipitated from the solution either by the addition of zinc shavings $2KAuCy_2 + Zn = K_2ZnCy_4 + 2Au$, or by electrolysis The gold is collected as a compact mass by fusion with sodium carbonate and charcoal

Gold Refining

Gold is refined by one of the following processes

1 **Electrolysis**—The anode is the alloy to be purified, the electrolyte is a solution of gold chloride in hydrochloric acid, and the cathode is pure gold. On electrolysis, fairly pure gold is deposited on the cathode, silver forms silver chloride which remains as a deposit about the anode

2 **Cupellation processes**—Gold is alloyed with an easily oxidizable metal, say lead The alloy of lead and gold is heated in a stream of air in a furnace with a shallow hearth made of bone ash The lead is oxidized to litharge, PbO, which is then partly blown from the surface of the molten metal, and partly absorbed by the bone ash When the gold appears as a bright disc, the operation is stopped and the gold removed If silver be present, silver and gold remain alloyed after the operation, and they must be separated by some other process—say "parting with sulphuric acid"

3 **Parting with sulphuric acid**—In the old process of parting silver and gold, known as quartation, an alloy of gold and silver, containing less than 25 per cent of gold, was treated with nitric acid The silver dissolved as silver nitrate, and the gold remained behind undissolved as a brown powder Parting with sulphuric acid is cheaper Here the alloy is boiled with concentrated sulphuric acid, then with nitric acid The gold is not attacked, and it remains behind as a brown porous mass This is washed, dried, and fused into a compact mass with sodium carbonate and charcoal

§ 8 Colloidal Gold and Silver

If a solution containing 0·01 to 0 001 per cent of gold chloride be made slightly alkaline by the addition of magnesia, and then a few drops of a reducing agent—formaldehyde, oil of turpentine, aqueous solution of acetylene, solution of phosphorus in carbon disulphide, carbon monoxide gas, sodium hyposulphite, $Na_2S_2O_4$, etc—be added, the solution

will probably acquire a ruby-red colour. Metallic gold is present in the form of minute particles which do not settle under the influence of gravity, and consequently remain suspended an indefinite time, and the solution can be filtered through paper unchanged The solution is sometimes called **Faraday's gold**, because it was studied by M Faraday in 1857 The gold is in colloidal solution because the clear solution appears opalescent by Tyndall's optical test, and the particles can be perceived by the ultramicroscope Similarly, by the action of certain reducing agents on soluble silver salts, Carey Lea (1887) obtained coloured solutions containing colloidal silver from which finely divided silver was obtained coloured golden-yellow, ruby, blue, etc

The metallic gold can be removed from its colloidal solution by shaking the solution with precipitated aluminium hydroxide, stannic hydroxide, barium sulphate The decolorization here resembles the decoloration of coloured solutions by shaking them with recently ignited charcoal The gold is absorbed by the precipitating agent Animal charcoal, if shaken with the solution, adsorbs the gold The addition of electrolytes—acids, neutral salts and alkalies—changes the red colour to blue, then violet, and then black This is due to the coagulation of the particles of gold into clots The gold then settles to the bottom of the fluid

When an insoluble precipitate is formed in the absence of electrolytes by a reaction between two chemical compounds, it is almost always in the colloidal condition Thus if aqueous hydrogen sulphide be added to a solution of arsenious acid, a turbid yellow solution of colloidal arsenic sulphide is formed $2H_3AsO_3 + 3H_2S \rightleftharpoons As_2S_3 + 6H_2O$ If the precipitate be made by adding an aqueous hydrogen sulphide to a solution of arsenious chloride, a coagulated precipitate of arsenious sulphide is formed In the latter case, hydrochloric acid is produced by the reaction: $2AsCl_3 + 3H_2S \rightleftharpoons As_2S_3 + 6HCl$ If some hydrochloric acid be added to colloidal arsenic sulphide formed as just indicated, the suspended colloid is at once coagulated and precipitated These facts illustrate a principle of great importance in quantitative analysis where successful work depends upon the formation of an insoluble precipitate which can be easily washed free from absorbed mother liquid When a colloid is precipitated by an electrolyte, as when aluminium and ferric hydroxides are precipitated by ammonia in the presence of ammonium chloride, the salt, ammonium chloride, coagulates the colloidal hydroxides into the gel condition During the washing of the gel precipitate, the gel passes into the sol condition, because the coagulating salt is removed by washing Hence a solution of ammonium nitrate is used for washing aluminium and ferric hydroxide precipitates in order to keep the colloid in the coagulated or gel condition. The ammonium nitrate is driven off during the ignition of the hydroxides Gel colloids are said to be **reversible colloids** when they can be converted into the sol condition by restoring the original conditions, *e g* by washing out the coagulating electrolyte from precipitated aluminium hydroxide On the other hand, **irreversible colloids** cannot be reconverted into the sol condition once they have passed into the gel condition, *e g* stannic hydroxide, gold, etc

Purple of Cassius.—If a mixture of stannic and stannous chlorides be added to a very dilute solution of gold chloride, hydrated stannic oxide is precipitated and the gold chloride is reduced to the metal. The

precipitate of stannic hydroxide may have tints varying from red to violet according to the concentration and composition of the solution This precipitate is called purple of Cassius because A. Cassius wrote a pamphlet —entitled *De Auro*—describing its preparation in 1685 The mode of making this substance was known to B Valentine in 1603, and to J R. Glauber, 1660 It was used at that time for colouring glass and enamels. The colour of purple of Cassius is due to the precipitation of finely divided gold on the stannic hydroxide Similar colours are made by precipitating gold on magnesium, calcium, and barium hydroxides, barium sulphate, zirconium oxide, alumina, lead sulphate, and china clay Purple of Cassius remains as a residue when alloys of gold, and tin with a large excess of silver, are treated with nitric acid, and when a gold tin alloy is vaporized in air The tin burns to stannic oxide, and it is at the same time stained by the condensation of the vapour of metallic gold. The old view that purple of Cassius is a compound of tin oxide and aurous oxide has been abandoned A "purple of Cassius" has been prepared with platinum in place of gold

§ 9 Copper, Silver and Gold—Oxides and Hydroxides

The three monoxides Cu_2O Ag_2O, and Au_2O, are here indicated in the order of their stability Cuprous oxide, Cu_2O, is the most stable of the copper oxides It is formed by heating copper or copper oxide in air to a high temperature, silver oxide, Ag_2O, decomposes between 250° and 300°, and aurous oxide, Au_2O, decomposes at about 250° Similar remarks apply to the hydroxides The heats of formation of copper and silver monoxides are Cu_2O, 40 8 Cals, Ag_2O, 5 9 Cals In spite of the fact that silver oxide is decomposed at a red heat, silver appears to unite with oxygen to form Ag_2O at about 1400°, and unless very rapidly cooled, it will decompose at the lower temperature This phenomenon is connected with the inversion of the thermal value of reactions at elevated temperatures previously discussed.

A series of well defined salts corresponding with Ag_2O are known—silver nitrate, $AgNO_3$, silver sulphate, Ag_2SO_4, etc With the exception of silver carbonate, Ag_2CO_3, these salts do not appear to be hydrolyzed by water Cuprous sulphite and cuprous thiosulphate—Cu_2SO_3 and $Cu_2S_2O_3$—are known, cuprous sulphate, Cu_2SO_4, probably exists in aqueous solutions of cupric sulphate in the presence of metallic copper $Cu + CuSO_4 \rightleftharpoons Cu_2SO_4$ This action, however, must be very slight at ordinary temperatures but in the case of ammoniacal solutions, a colourless crystalline salt, $Cu_2SO_4 \, 4NH_3 \, H_2O$, has been isolated If methyl sulphate, $(CH_3)_2SO_4$, be brought in contact with cuprous oxide, in the absence of water, at 160°, cuprous sulphate is formed $(CH_3)_2SO_4 + Cu_2O = Cu_2SO_4 + (CH_3)_2O$ The salt is washed with ether, and it is fairly stable if moisture be absent With hydrochloric acid, cuprous chloride, $CuCl$, is formed, with dilute nitric acid, cupric nitrate, and with sulphuric acid, cupric sulphate, and aurous oxide, Au_2O, like cuprous oxide, exhibits little tendency to form salts. Aurous sulphite and aurous thiosulphate have been reported, but they are probably solutions of colloidal gold reduced by sulphur dioxide or by thiosulphate

Cuprous oxide is precipitated when an aqueous solution of an alkaline cuprous salt is reduced by glucose or by an arsenite, and it is also

precipitated as a yellow powder when an alkaline hydroxide is added to a cuprous salt. Silver salts under the same conditions give a chocolate-brown powder which is somewhat hydrated. It is not silver hydroxide, AgOH, but is probably argentous oxide, Ag_2O. It is slightly soluble in water (one part of the oxide dissolves in nearly 3000 parts of water), the solution has an alkaline reaction and metallic taste. Silver oxide is reduced by hydrogen peroxide to metallic silver, and it rapidly oxidizes sulphur, red phosphorus, arsenic sulphide, and antimony sulphide often with incandescence. Both silver and copper monoxides—Ag_2O and Cu_2O—when precipitated by ammonia, are soluble in an excess of the reagent. On standing, the silver oxide solution deposits black shining crystals of "fulminating silver," which is explosive, particularly when dry. It is often stated to be silver nitride, Ag_3N. Aurous hydroxide, AuOH, is said to be formed when potassium hydroxide is added to aurous bromide. The violet-brown coloured solution may contain aurous oxide in colloidal suspension. The coagulated powder is slightly soluble in water and in alkalies. It is decomposed by hydrochloric acid.

Cupric oxide, CuO, is formed as a black hygroscopic powder when copper is heated in air or in oxygen, or by the calcination of copper nitrate, carbonate or hydroxide. When heated to a high temperature, cupric oxide cakes, fuses, and decomposes giving a mixture of cuprous and cupric oxides and finally cuprous oxide. Cupric oxide, when heated is reduced to the metal by reducing agents—hydrocarbons, carbon monoxide, hydrogen, etc. When an alkaline hydroxide is added to a cold solution of a cupric salt, pale blue cupric hydroxide, $Cu(OH)_2$, is precipitated. If the liquid be boiled a black substance is formed, possibly a mixture of $Cu(OH)_2$ and Cu_2O. It is difficult to wash away the alkalies from the blue precipitate. Boiling water converts it into cupric oxide. The blue precipitate is soluble in an excess of alkali, forming a blue solution. The solution of cupric hydroxide, $Cu(OH)_2$, in aqueous ammonia is called *Schweitzer's reagent*. It dissolves cellulose (cotton wool, filter paper, etc.). A cellulose like substance is reprecipitated when the solution is acidified with hydrochloric acid.

Auric oxide, Au_2O_3.—Silver has been reported to form an oxide corresponding with cupric oxide. When a solution of potassium hydroxide is added to a boiling solution of gold chloride a brown powder—auric oxide, Au_2O_3—is precipitated. If the solution is cold, an orange-coloured precipitate of auric hydroxide, $Au(OH)_3$, separates. This is dehydrated at 100°, forming AuO.OH, at 160°, a dark chestnut-brown auro auric oxide, AuO, is formed; and finally auric oxide, Au_2O_3. At 250° auric oxide decomposes into its elements. Auric hydroxide is soluble in an excess of alkali, forming a complex salt, potassium aurate, $KAuO_2$, which is precipitated by the addition of nitric acid. The aurates are crystalline salts somewhat unstable, and soluble in water. Auric oxide is almost always acidic, and hence it is sometimes called auric acid. Under special conditions it shows feebly basic properties, forming unstable oxy-acid salts like auric nitrate, $Au(NO_3)_3$, and auric sulphate, $Au_2(SO_4)_3$. The oxide AuO is supposed to be an aurous aurate—$Au.AuO_2$. Auric oxide, Au_2O_3, dissolves in hydrochloric acid, forming a complex acid—hydrochloroauric acid, $HAuCl_4$—which forms a series of complex salts, chloroaurates. The chloride $AuCl_2$ is supposed to be aurous chloroaurate,

$Au.AuCl_4$ When a solution of gold chloride is treated with ammonia, a yellow precipitate of explosive "fulminating gold" is obtained Its molecular composition is somewhat uncertain, its empirical composition is said to be $AuN_2H_3\ 3H_2O$

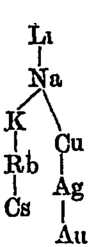
Copper is said to form a copper quadranto oxide, Cu_4O, according to Rose, when an alkaline solution of cupric chloride is reduced with an alkaline stannous chloride, and silver is said to form silver quadranto-oxide, Ag_4O, when silver citrate is reduced in a current of hydrogen at 100°, extracted with water, and treated with potassium hydroxide The evidence is indecisive Gold, apparently, does not form a similar sub oxide, although some say that Au_2O exists The alleged suboxides may be mixtures of the respective metals with higher oxides

Copper dioxide, CuO_2, is formed as a yellowish brown powder when a dilute solution of hydrogen peroxide acts upon cupric hydroxide The product prepared in aqueous solution is always impure owing to hydrolysis, and ethered alcoholic solutions are preferred The compound is unstable, and when treated with dilute acids, it gives a cupric salt and hydrogen peroxide Hence it is probably a superoxide

Silver peroxide, Ag_2O_2 —The black powder which collects at the anode when silver nitrate is electrolyzed is considered to be silver pernitrate, $AgNO_4$, or a mixture of this with silver peroxide The product soon decomposes, forming a silver peroxide When dissolved in acids, silver peroxide gives oxygen or ozone, and when slowly acted upon by water it gives hydrogen peroxide $Ag_2O_2 + H_2O = Ag_2O + H_2O_2$ Hence Mendeleeff would consider it to be a superoxide Ag—O—O—Ag Silver peroxide dissolves in aqueous ammonia with the evolution of nitrogen $3Ag_2O_2 + 2NH_3 = 3Ag_2O + 3H_2O + N_2$ Gold does not give a peroxide When potassium persulphate reacts with silver phosphate, argentic oxide with the ultimate composition AgO is formed This does not give hydrogen peroxide with acids, and it appears to be a basic oxide resembling cupric oxide, CuO The same oxide seems to be formed when silver is used as anode in the electrolysis of water in an alkaline solution If the solution be acid, a silver sesquioxide, Ag_2O_3, is said to be formed

§ 10 The Family Relationship of Copper, Silver, and Gold

These three elements are generally classed together in so called "systematic chemistry," and they are furthermore considered to be related with the alkali metals The copper group of elements is generally linked with the alkali metals by the scheme indicated in the margin, which starts with the elements with the lowest atomic weights The fault with the scheme is that it makes the relationship appear far closer than is indicated by known facts If we recall the relationship between the members of, say, the alkali metals, and the halogen families, the relationship between the individual members of this so called family and with the alkali metals is strikingly obscure The student might well inquire why these elements are grouped together at all, and cogent reasons might be urged for grouping gold with platinum, silver with palladium, and copper with mercury The reason why this is not done will appear when we take a general survey of *all* the elements



Returning to the elements copper, silver, and gold, the physical properties may be tabulated

TABLE XXVI —PHYSICAL PROPERTIES OF COPPER, SILVER, AND GOLD

——	Copper	Silver	Gold
Atomic weight	63 6	107 88	197 2
Specific gravity	8 93	10 49	19 265
Atomic volume	7 07	10 20	10 11
Melting point	1082 6°	960 0°	1062 4°
Boiling point	2310°	1955°	2200°
Latent heat of fusion (cals)	43	24 36	16 3
Specific heat	0 086	0 055	0 030

In malleability, ductility, and tenacity, silver is intermediate between copper and gold While the large atomic volume of the alkali metals was associated with great chemical activity and affinity for oxygen, the low atomic volume of these elements is related with their weak affinity for oxygen, etc Copper, for instance, is alone oxidized in air The oxides of copper, silver, and gold are easily reduced, while the oxides of the alkali metals are reduced with great difficulty The reduction of copper, silver, and gold by magnesium is the more energetic the greater the atomic weight of the metal—cuprous oxide reduces easily silver oxide reduces with explosive violence, and gold oxide breaks down into its constituents below the ignition point of magnesium Silver appears to be uni-, bi-, and ter-valent, but copper is both uni- and bi valent, and gold is uni- and ter-valent Hence these three elements have univalency in common with the alkali metals Cupric salts are isomorphous with iron, cobalt, and nickel. The isomorphism of the silver and sodium sulphates and selenates indicates a relationship of some kind between silver and sodium. The alkali halides, like silver chloride and bromide, crystallize in the cubic system—silver iodide crystallizes in the hexagonal system and the crystals pass into the cubic system at about 146°—on cooling the reverse change takes place—sometimes with explosive violence Silver seems to be related with copper through argentic oxide, AgO, where silver appears to be bi-valent, silver pyridine persulphate, $Ag_2S_2O_8$ 4Py is isomorphous with the analogous copper pyridine persulphate, CuS_2O_8 4Py, with gold, through silver sesquioxide, Ag_2O_3, and with the alkalies through argentous oxide, Ag_2O, and with the magnesium family through mercury The more salient differences between copper and the alkali metals are (1) The elements of the alkali metals have a small density, the other metals have a large density, (2) the alkali metals do not occur free, (3) the elements of the alkali metals are chemically active, the others not so, (4) the haloids of the alkalies are all soluble in water, and are not hydrolyzed by water, copper and silver form sparingly soluble haloids, and the haloids of copper and gold, not silver, are hydrolyzed by water (5) The oxides and hydroxides of the alkalies are strongly basic, the oxides and hydroxides of copper and gold are feebly basic, and they accordingly form basic salts (6) The alkali metals do not form complex salts, whereas copper, silver, and gold, form many complex salts.

Questions

1 Describe the successive phenomena observed when ammonium hydroxide solution is added, drop by drop to a solution of cupric sulphate and indicate by formulæ or equations the nature of the changes which occur —*Massachusetts Polytechnic Inst*, *U S A*

2 —(*a*) In the laboratory you passed dry hydrogen over copper oxide which was heated in a tube How does this experiment illustrate an analytical reaction, a synthetic reaction, oxidation and reduction? (*b*) If you started with an unknown mixture of copper oxide and copper, say 10 grams, and after heating and passing hydrogen over it the resulting weight of pure copper was 9 2 grams how much of the original weight of the 10 grams was copper oxide and how much was metallic copper?—*Worcester Polytechnic Inst U S A*

3 —(*a*) Show the analogy between the reactions of copper on nitric acid and copper on sulphuric acid (*b*) What products are formed from the concentrated sulphuric acid when the latter is warmed with potassium iodide? (*c*) What reason have you for thinking that no nascent hydrogen is formed in the reactions mentioned under (*a*)?—*Amherst Coll U S A*

4 It is desired to obtain pure copper nitrate, the only source of copper at hand being a complex solution of lead cadmium, copper, and mercurous nitrates Using this solution as the source of the copper, how may a new solution of copper nitrate be prepared?—*Massachusetts Inst of Technology U S A*

5 An unknown quantity of potassium bromoaurate $KAuBr_4$ on being heated, left 9 9245 grams of a mixture of metallic gold and potassium bromide The mass on being treated with water left 6 18997 grams of gold The solution of KBr required 3 38510 grams of silver for total precipitation by Stas' method, and afforded 5 89143 grams of silver bromide These data afford three independent values for the atomic weight of gold which you are required to calculate ($K = 39\ 03$, $H = 1$, $O = 15\ 96$ $Br = 79\ 76$, $Ag = 107\ 66$) —*Science and Art Dept*

6 What takes place when hydrogen is passed over red hot copper oxide? How has this reaction been applied to determine (*a*) the composition of water, (*b*) the atomic weight of copper? What special precautions must be observed in each case in order to obtain accurate results?—*London Univ*

7 A chemical manufacturer gives out a kilogram of metallic silver to be made into silver chloride how much silver chloride ought to be returned by the workman, supposing the average yield is 99 8 per cent of the theoretical?

CHAPTER XXII

SULPHUR AND ITS HYDROGEN COMPOUNDS

Atomic weight, $S = 32\ 07$, molecular weight of solid, $S_8 = 256\ 56$, of vapour at 1000°, $S_2 = 64\ 14$ Melting point of rhombic sulphur, 113°–115°, monoclinic sulphur, 119°–120°, boiling point, 444 7° Relative vapour density depends on temperature (air = 1), 6 6 to 2 2

§ 1 Sulphur—Occurrence and Preparation.

THE element sulphur has been known from the beginning of history It is mentioned in the Bible and in Homer It was placed among the elements by Lavoisier, but for some time previously it was regarded as "the principle of fire" The name is derived from the Sanscrit *sulveri* through the Latin *sulphurium*

Occurrence —Sulphur is widely distributed in nature both as free and as combined sulphur Deposits of free or native sulphur occur in volcanic districts, Iceland, Italy (Romagna, Marken, Tuscany, Campania, and Calabria), Sicily (chiefly in the south), Greece (Island of Milo), Russia, Austria-Hungary (Radoboj and Swoscowice), South France, Spain, Asia Minor, Persia, India, Palestine, Algeria, Morocco, Japan (Sulphur Island) New Zealand (White Island, etc), United States (Louisiana, Oregon, Utah, Nevada, Wyoming, Texas), Mexico (Popocatapetl), Chili, Peru, etc

There are two main types of native sulphur (1) *The solfataric type* [1] found in lava fissures and in extinct volcanic vents (Japan, Mexico) Deposits of this type are forming at the present day in volcanic districts from the mutual action of hydrogen sulphide and sulphur dioxide which occur among volcanic gases (2) *The gypsum type* The sulphur appears to have been liberated from gypsum by the reducing action of bituminous matters found associated with the gypsum Calcium sulphide is probably formed from the sulphate, and this, by the action of water and carbon dioxide forms sulphur, calcium carbonate and hydrogen sulphide The Sicilian deposits and perhaps the more important sulphur deposits are of this type

Sulphur is also a product of the life action of certain bacteria—*Beggiatoa alba* and *Chromatium Okeini* Just as plants and animals derive energy and heat by the oxidation of carbon, so do these bacteria appear to get their energy and heat by the oxidation of sulphur It is estimated that 25 per cent of their body is sulphur The sulphur occurs in the bodies of some varieties as small granules The bacteria theory of the origin of sulphur assumes that some sulphur beds have been formed by these organisms

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[1] Solfatara—a volcanic vent or volcanic area which gives off sulphurous vapours, steam, etc , and which probably represents the last stages of volcanic activity

Many important metallic ores are sulphides, that is, compounds of sulphur with one or more metals. Thus, *galena* (lead sulphide, PbS), *zinc blende* (zinc sulphide, ZnS), *cinnabar* (mercury sulphide, HgS), *stibnite* (antimony sulphide, Sb_2S_3), *copper pyrites* (Cu_2S, Fe_2S_3), *iron pyrites* (iron sulphide, FeS_2), etc. Some important sulphates also contain sulphur, *e.g.* *gypsum* (calcium sulphate, $CaSO_4$), *heavy spar* (barium sulphate, $BaSO_4$), etc.

Sulphur occurs in many organic compounds, and in animal and vegetable products: onions, garlic, mustard, horseradish, hair, many oils, eggs, proteids, etc. Hydrogen sulphide is found in the water of many sulphur springs.

The extraction of crude sulphur.—A little sulphur is obtained from iron pyrites; from the by-products in Leblanc's soda process (*q.v.*), and from the spent oxide of gasworks (*q.v.*). Probably 90 per cent. of the sulphur used in the world comes from Sicily, and Louisiana. The "sulphur earth" in Sicily occurs in lodes mixed with limestone and gypsum. The amount of sulphur in "workable" ore varies from 8 up to about 25 per cent.

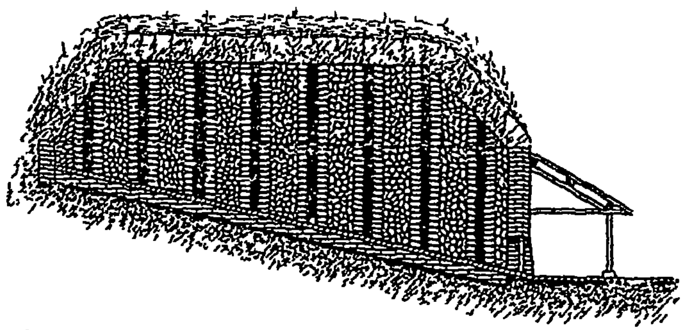


FIG. 147.—Calcarone or Sulphur Kiln (Diagrammatic Section).

The sulphur is separated by heating the ore, and allowing the molten sulphur to flow away from the mineral impurities. This is effected by stacking the ore on the sloping floor, Fig. 147, of a circular kiln without a permanent roof. The kilns are called calcaroni. In stacking the ore, air spaces are left at intervals to serve for ventilation. The stack is covered with powdered or burnt ore. The sulphur is ignited near the bottom. A portion of the sulphur acts as fuel, and melts the remainder which collects at the lowest point of the inclined bottom of the kiln. After about five days, a plug at the lower end of the kiln is removed, and the sulphur is run into small wooden moulds. The opening is closed to be reopened day by day until, in from three to five more days, the sulphur ceases to flow.

About one third of the sulphur is lost in the calcarone system of extraction. It is, however, cheaper to use the sulphur as a fuel than to import coal. The loss, however, is excessive even then, and in consequence, the calcarone method is being displaced by more economical kilns—Gill's kilns—which are worked in sets. The products of combustion from one kiln pass into the adjacent kiln and there do some work before escaping into the atmosphere. In H. Frasch's method (1891), used at Louisiana, the sulphur is melted *in situ*. Pipes are driven into the sand and superheated water is forced into the lode. The molten sulphur

collects in a central well from which it is raised to the surface by compressed air

The purification or refining of crude sulphur.—The crude sulphur from the kilns—also called "brimstone"—is graded and put on the market It may be afterwards purified by distillation from a retort which opens into a large brickwork chamber The sulphur vapour condenses in the chamber The first lot of vapour sublimes as a light powder on the walls. This powder is called *flowers of sulphur* As the condensing chamber gets hot, the condensed sulphur melts and collects on the floor as a liquid which is drawn off from time to time and cast into large wooden moulds—*rock sulphur*, or in cylindrical wooden moulds—*roll sulphur*

Uses.—Crude sulphur is used in making sulphur dioxide for bleaching straw, wool, etc, for the manufacture of sulphites for bleaching wood fibres, etc, and for the manufacture of sulphuric acid It is also used in making carbon disulphide Purified sulphur is used in making gunpowder, matches, colours, vulcanite, etc, and also medicinally Flowers of sulphur is used as an insecticide and fungicide

§ 2 Rhombic, Octahedral, or α-Sulphur.

Ordinary sulphur is a pale yellow brittle solid, without taste or smell At − 50° the sulphur is almost colourless Sulphur is commonly found in rhombic or octahedral crystals with a specific gravity varying from 2·03 to 2·06 It is a bad conductor of heat and electricity If a stick of roll sulphur be held in the hand it begins to crackle and breaks owing to unequal expansion by the heat Sulphur is practically insoluble in water, sparingly soluble in alcohol and glycerine, more soluble in essential oils, and readily soluble in sulphur chloride, S_2Cl_2, and carbon disulphide, CS_2 For instance, 100 grams of carbon disulphide at 0° dissolve 22 grams of sulphur, at 20°, 41·8 grams and at 40°, 100 grams If the solution in chloroform or carbon disulphide be allowed to stand at ordinary temperatures, crystals of sulphur are deposited as *the solvent evaporates* The appearance of the crystals is shown by the photograph, Fig 148 An ideal crystal is sketched in outline About 60 or 70 per cent of flowers of sulphur consists of these crystals Native sulphur also occurs in this form The crystals are quite stable at ordinary temperatures This crystalline form of sulphur is called "α sulphur," "rhombic sulphur," or "octahedral sulphur" Nearly thirty different crystalline modifications of the rhombic type of crystalline sulphur have been reported And this

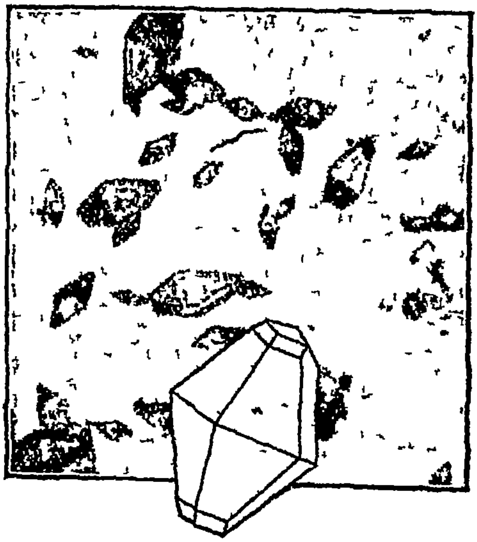


FIG 148.—Rhombic or α sulphur

fact leaves us some misgivings about the rigid exactness of R J Hauy's law (p 173)

Sulphur unites with oxygen when heated in air It ignites at about 363°, and at about 282° if heated in oxygen The vapour of sulphur ignites at about 285° in air At 100° sulphur is oxidized in oxygen gas at a measurable rate Oxidation, even at ordinary temperatures, can be detected Finely divided sulphur oxidizes slowly in moist air, forming sulphurous and sulphuric acids Hence these two acids can nearly always be detected in commercial flowers of sulphur, while roll sulphur is almost free from these acids Sulphur also unites readily with many metals, forming sulphides Heat is usually required to start the reaction The combination is often attended with incandescence Examples with iron and zinc have been indicated on p 20 A strip of copper introduced into the vapour of sulphur enters into combination with vivid combustion. Sulphur combines with carbon at a red heat, forming carbon disulphide —CS_2, with chlorine at the boiling point of sulphur, and with hydrogen at the same temperature

§ 3 Monoclinic, Prismatic, or β-Sulphur

In 1823 E Mitscherlich announced the fact that the element sulphur can be crystallized in two distinct forms, and concluded that a substance, whether simple or compound, may assume two different crystalline forms, p 179 If, say, 500 grams of sulphur be melted in a clay or porcelain crucible and the mass allowed to stand until a surface crust is formed, beautiful long prismatic needle-like crystals of waxy yellow sulphur will be found to have grown on the walls of the crucible, and on the underside of the crust when the crust is pierced, and the still fluid sulphur is poured away These monoclinic prisms of sulphur have many properties different from ordinary rhombic sulphur just discussed The specific gravity, for instance, is 1 93, instead of 2 04, and the melting point is 120° in place of 115° Both varieties are soluble in carbon disulphide Some crystals of monoclinic sulphur are illustrated in Fig 149 along with an outline sketch of an ideally perfect crystal This form of sulphur is called "β sulphur," "monoclinic sulphur," or "prismatic sulphur"

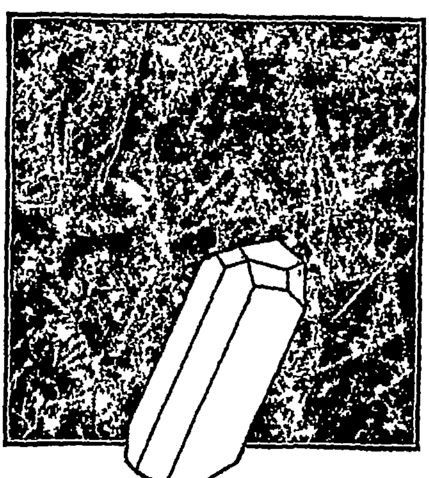


FIG 149 —Monoclinic or β sulphur

In about a day's time, the monoclinic prisms become light yellow, opaque, brittle, and crumble into powder at the slightest touch The grains of powder are small rhombic crystals of α sulphur If the rhombic crystals be kept a few hours between 108° and 112°, they also become

opaque and change to a friable crumbling mass of monoclinic prisms The two reactions are thus reversible Experiment shows that the monoclinic prisms are unstable below 94 5°, and slowly pass into the rhombic variety The change is accelerated by wetting the monoclinic prisms with carbon disulphide, or by bringing the monoclinic sulphur in contact with a crystal of the rhombic variety Conversely, the rhombic sulphur is unstable above 94 5°, and slowly passes into the monoclinic variety With the notation previously employed, the change is symbolized

$$S_{\text{rhombic}} \overset{94\ 5^\circ}{\rightleftharpoons} S_{\text{monoclinic}}\,,\ \text{or}\ \alpha S \overset{94\ 5^\circ}{\rightleftharpoons} \beta S$$

Hence, 94 5° is a transition temperature.

The monoclinic crystals just indicated were studied by E Mitscherlich in 1823 There are, however, two other varieties of monoclinic crystals with angles somewhat different from the variety just indicated. In 1884, D Gernez prepared what he called "soufre nacré," nacreous sulphur—from the French *nacre*, mother-of-pearl—as follows —

FIG 150 —Nacreous Sulphur

Heat sulphur in a sealed tube with benzene, or toluene, carbon disulphide, alcohol, etc , so that there is no undissolved sulphur in the tube when the tube is hot Then immerse one end of the tube in a freezing mixture formed, say, by dissolving ammonium nitrate in cold water Long nacreous flakes separate at the cold end of the tube and gradually extend into the remaining solution

An ideal monoclinic crystal of nacreous sulphur is illustrated in Fig 150 Similar crystals were made by E Mitscherlich in 1823 by the following method —

Saturate an alcoholic solution of sodium sulphide with sulphur, filter off the clear reddish coloured supernatant liquid, and, after adding a little more alcohol, let the solution stand for some time Needle like crystals of nacreous sulphur grow from the surface of the solution

W Muthmann (1890) noticed that in preparing nacreous sulphur by the method just indicated, hexagonal plates—tabular sulphur—sometimes separate from the solution when the temperature is about 5°, but not about 14° These crystals also belong to the monoclinic system An ideal crystal is illustrated in Fig 151 Although the three types of crystals just named belong to one system, the interfacial angles are not the same Thus, the angle between two important faces of one of the crystals depicted in Fig 149 is 84° 14′, with similar faces of the nacreous crystals, Fig 150, 88° 13′, and with tabular crystals, Fig 151, 75° 58′

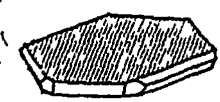


FIG 151 —Tabular Sulphur

The rhombic crystals (Fig 148) are sometimes called Muthmann's S_I, the monoclinic crystals (Fig 149), Muthmann's S_{II}, the nacreous crystals (Fig 150), Muthmann's S_{III}, and the tabular crystals (Fig 151), Muthmann's S_{IV} In addition to the crystalline varieties of sulphur just considered, two others, of no particular importance in our present study, have been reported, namely, G Friedel's *triclinic sulphur* (1879), and R Engel's *rhombohedral sulphur* (1891) When an element or compound exists in two or more crystalline forms it is said to be polymorphous—from the Greek πολύς (polus), many, and μορφή (morphē), form Hence

sulphur is polymorphous If a substance exists in two different crystalline forms, it is said to be dimorphous—from the Greek δίς (dis), twice. Ammonium nitrate and calcium carbonate are examples.

§ 4 Sulphur and the Phase Rule

By plotting the vapour pressure curve of rhombic sulphur at different temperatures, we get the curve PO_1, Fig 152, similarly, by plotting the vapour pressure curve of monoclinic sulphur, we get the curve O_1O_2, this variety of sulphur melts at 120°, however, by continuing the vapour pressure curve of the liquid, we get O_2Q By plotting the transition points of rhombic sulphur at different pressures, we get the curve O_1O_3, and by plotting the melting point of monoclinic sulphur at different pressures, we get the curve O_2O_3 Monoclinic sulphur cannot exist at pressures higher than that represented by the point O_3 The continuation of the curve O_3N represents the effect of pressure on the melting point of rhombic sulphur This diagram, Fig 152, should be compared with Fig 56 for water In Fig 152, we have the additional complication corresponding with the two forms of sulphur now under consideration The phase rule enables us to form a very clear idea of the conditions of equilibrium When the condition of the system is represented by a pressure and temperature corresponding with one of the three triple points—O_1, O_2, O_3—the system is invariant, and any change in temperature or pressure will lead to the suppression of one of the three phases, points on one of the curves—PO_1, O_1O_2, O_2Q, etc —represent univariant systems, and points in one of the three regions—PQ, QO_2N, NO_1P—represent bivariant systems It will of course be obvious that we are here dealing with the one component sulphur, and four possible phases—sulphur vapour and liquid, and rhombic and monoclinic sulphur Can all four phases exist under any conditions of temperature and pressure in a state of equilibrium? According to the phase rule, the variance of such a system will be $1 - 4 + 2 = -1$ This is an impossible value Such a system would not be in a state of true equilibrium The metastable states, or states of false equilibrium are interesting The QO_2 and the PO_1 curves meet at a point corresponding with the temperature 114 5° This is the melting point of rhombic sulphur If the transformation of rhombic to monoclinic were very fast, it would be impossible to state the melting point of rhombic sulphur, because it would pass into the monoclinic form before a determination could be made The upward left-to-right slopes of the curves O_1O_3 and O_2O_3[1] correspond with the fact that the melting point of sulphur is raised by increasing pressures The converse was true in the case of ice, Fig 56, and in consequence, the corresponding curve sloped the opposite way

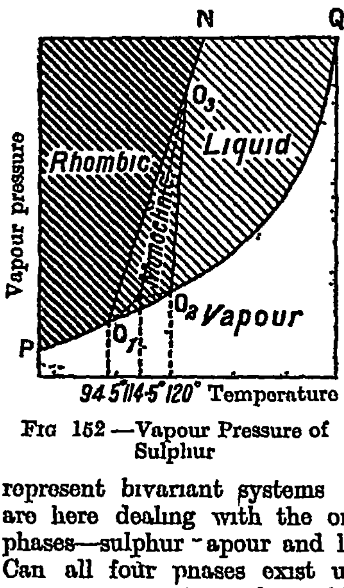


FIG 152 —Vapour Pressure of Sulphur

[1] These curves are exaggerated in the diagram That, however, does not affect the principles under discussion.

§ 5 Amorphous or Colloidal Sulphur.

Sulphur exists in at least two different colloidal or amorphous conditions in which no signs of crystallization can be detected under the microscope. The term amorphous is derived from the Greek ἀ, without, μορφή (morphē), form One of the amorphous forms is soluble in carbon disulphide, the other is not If hydrogen sulphide be passed into a saturated aqueous solution of sulphur dioxide at 0°, or if an alcoholic solution of sulphur be poured into water, or if a saturated solution of sodium thiosulphate be mixed with twice its volume of concentrated hydrochloric acid, and cooled to 10°, colloidal, soluble, or δ-sulphur is formed

Action of heat—Sulphur is pale yellow at ordinary temperatures, and almost colourless at −50°, and at 100° it is intense yellow If a piece of ordinary rhombic sulphur be gradually heated in a test-tube, the sulphur crackles and falls to pieces as indicated above As the temperature rises, the sulphur melts to a clear, limpid, amber coloured liquid between 113° and 115°, the colour darkens, and the liquid loses its mobility, until, at about 162°, the mass is almost black, and so viscid that the test-tube can be turned upside down without pouring out the sulphur The viscosity reaches a maximum at about 180°, for as the temperature rises still higher, the dark colour remains, but the mass becomes more and more mobile until, at 444 5°, the liquid begins to boil, forming a reddish orange vapour If the liquid be allowed to cool, the sulphur undergoes the same changes, but in the reverse order If the vapour be heated still higher, it becomes deep red at 500°, and straw-yellow at about 650°

Molten sulphur—λ- and μ-sulphur—If sulphur, heated to about 350°, be poured into cold water, a tough elastic material resembling indiarubber—called plastic sulphur—is obtained Plastic sulphur is also obtained by distilling ordinary sulphur from a glass retort and allowing the distilled liquid sulphur to flow into cold water A long continuous thread of plastic sulphur is then obtained. The specific gravity of plastic sulphur is about 1 95, nearly the same as monoclinic sulphur, but unlike the crystalline varieties, this form of sulphur can be moulded between the fingers, and drawn into somewhat elastic threads Plastic sulphur is a supercooled liquid which has been hurried past its crystallizing temperature and cooled so low that it has formed a viscid mass The case is analogous with that studied on p 166—supercooled sodium thiosulphate Plastic sulphur slowly[1] crystallizes on standing The change is accelerated by rubbing the mass, and is fairly rapid if the mass be heated to about 100° The latent heat of solidification—corresponding with about 9 4 Cals per kilogram—is evolved when the plastic or supercooled sulphur crystallizes Amorphous "solids" are in nearly every case to be regarded as supercooled liquids which have not taken up the stable crystalline condition

If α-sulphur be melted at a low temperature, and the pale yellow liquid be suddenly chilled, the crystalline product is almost completely soluble in carbon disulphide, while, as indicated above, if the dark brown liquid which is obtained when sulphur is heated to a higher temperature, be similarly treated, it forms an amorphous mass almost all insoluble in

[1] A trace of iodine retards the action

carbon disulphide It is therefore inferred that molten sulphur contains a mixture of two varieties of sulphur—the pale yellow mobile fluid, called λ sulphur, and the dark brown viscid fluid called μ sulphur When λ sulphur solidifies it forms crystalline α or β sulphur soluble in carbon disulphide, and when μ sulphur solidifies it forms an amorphous plastic mass insoluble in carbon disulphide The proportion of sulphur soluble and insoluble in carbon disulphide in solidified sulphur depends on the relative amounts of S_λ and S_μ present in the fluid at the time of solidification Experiment shows that there is a definite relation between the relative amounts of the two varieties present in a system in equilibrium at a definite temperature Thus, molten sulphur at 114 5°, if suddenly congealed, furnishes a mass which contains the equivalent of 3 7 per cent of μ sulphur, and 94 3 per cent of λ sulphur Ordinary plastic sulphur contains the equivalent of about one per cent. of λ sulphur and 99 per cent of μ-sulphur Ordinary rhombic sulphur has about 3 4 per cent. of the first variety, and it is estimated that if the latter were absent the melting point would be 119 25°, not 114 5°, similarly with monoclinic sulphur, the melting point would be raised a couple of degrees The proportion of μ-sulphur appears to increase with rising temperatures, and for each temperature there appears to be a definite equilibrium constant corresponding with the reversible reaction $S_\lambda \rightleftharpoons S_\mu$ The system takes some time to attain equilibrium under any given conditions The presence of sulphur dioxide and hydrogen chloride retard, while ammonia accelerates the speed of the change We may thus summarize the action of heat on the different forms of sulphur

$$\underbrace{S_\alpha \overset{94\ 5^\circ}{\rightleftharpoons} S_\beta}_{\text{Solid}} \overset{120^\circ}{\rightleftharpoons} \underbrace{S_\lambda \overset{160^\circ}{\rightleftharpoons} S_\mu}_{\text{Liquid}} \overset{444\ 5^\circ}{\rightleftharpoons} \underbrace{S_8 \overset{1000^\circ}{\rightleftharpoons} S_2}_{\text{Vapour}}$$

Amorphous sulphur soluble and insoluble in carbon disulphide — Let slaked lime be boiled with water and sulphur for some time After

TABLE XXVII —VARIETIES OF SULPHUR (To face page 401)

	Variety	Carbon disulphide	Water	Sp gr	Synonyms
Crystalline	Rhombic	Soluble	Insol	2 04	Octahedral S, α S, Muthmann's S_I
	Monoclinic needles	Soluble	Insol	1 93	Prismatic S, β S, Muthmann's S_{II}
	Monoclinic nacreous	Soluble	Insol	—	Nacreous S Muthmann's S_{III}
	Monoclinic tabular	Soluble	Insol	—	Tabular S Muthmann's S_{IV}
Colloidal	Amorphous	Soluble	Insol	—	
	Amorphous	Insol	Insol	1 955	γ sulphur
	Soluble	Soluble	Soluble	—	δ sulphur
Fluid	Fluid λ S				Solidifies to soluble amorphous or crystalline S
	Fluid μ S				Solidifies to insoluble amorphous S

the mixture has stood to allow the insoluble matters to settle, decant the clear reddish solution of calcium polysulphide Add a little hydrochloric acid. Calcium chloride is formed, and finely divided *milk of sulphur* is precipitated The sulphur remains suspended in the liquid for a long time on account of its very fine state of subdivision This sulphur is pale yellow in colour, it is said to contain a non-crystalline variety of sulphur soluble in carbon disulphide A certain amount of the variety (sp gr 1 955) insoluble in carbon disulphide is formed at the same time, this has been called γ-sulphur Several other sub-varieties of amorphous sulphur are known These are more or less closely related to the leading types just considered A complete and satisfactory statement of the different varieties of crystalline and amorphous sulphur is not yet possible. Those indicated above are tabulated on p 400 (Table XXVII)

§ 6 The Atomic and Molecular Weights of Sulphur.

1 **Combining weight**—J B Dumas (1859) and J S Stas (1867) heated silver in a tube through which a current of sulphur vapour was passed The excess of sulphur was distilled off in a current of carbon disulphide. The resulting silver sulphide was weighed It was found that 100 grams of silver gave 114 85 grams of silver sulphide Hence Ag S = 100 . 14 85 The combining weight of silver (oxygen = 8) is 107 88, hence the combining weight of sulphur is 16 035 Results not very different have been obtained by reducing a known amount of silver sulphide in a current of hydrogen, by finding the amount of silver in silver sulphate, by converting silver sulphide into silver chloride, and by converting sodium carbonate into sodium sulphate (T W Richards, 1891)

2 **Atomic weight**—Applying the method indicated on p 62, namely, collecting together a number of volatile compounds of sulphur whose vapour density is known, we obtain

TABLE XXVIII—VAPOUR DENSITIES OF SOME VOLATILE SULPHUR COMPOUNDS

Volatile compound	Vapour density H = 2	Composition molecular weight=vapour density	Amount of sulphur in the molecule
Hydrogen sulphide	34 07	Sulphur 32 07, hydrogen 2 016	32 07
Sulphur dioxide	64 07	Sulphur 32 07, oxygen 32 07	32 07
Sulphur trioxide	80 07	Sulphur 32 07, oxygen 48 0	32 07
Sulphur	64 14	Sulphur 64 14	64 14
Carbon disulphide	76 14	Sulphur 64 14, carbon 12 0	64 14
Phosphoric sulphide	222 35	Sulphur 160 35, phosphorus 62 0	160 35

The smallest amount of sulphur entering into the composition of any of these molecules lies somewhere between 32 01 and 32 14, the best representative value is taken to be 32 07 when hydrogen is 1 008, oxygen, 16, carbon, 12 0, phosphorus, 31 0 Hence this number represents the atomic weight of sulphur This result is confirmed by accurate determinations of the density of sulphur dioxide This is 64 07 Hence if oxygen be 16, sulphur must be 32 07

3 **Molecular weight**—At about 500° the vapour density of sulphur is nearly 6 6 (air = 1) This corresponds with the molecule S_6 By

raising the temperature or reducing the pressure the vapour density gradually diminishes until, at 1000°, it reaches 2 2, corresponding with the molecule S_2 The vapour density then remains constant, up to about 1700°, at about 2000° the vapour density corresponds with a partial dissociation of S_2 into atoms S, thus resembling the behaviour of iodine above 1000° It may be that at temperatures intermediate between 1000° and 500°, some or all of the molecules S_8, S_6, S_4, and S_2 are present, but the curve is steadily depressed with rising temperatures, and it shows no signs of flattening such as might be expected if any particular type of molecule predominated throughout any particular range of temperature This is illustrated by the graph of the vapour density of sulphur at different temperatures shown in Fig 153 The freezing and boiling point methods for the determination of molecular weights, indicated by examples pp 217 and 218, show that the molecule of sulphur is S_8 H. Erdmann (1908) represents the molecules of the two different forms of crystalline sulphur graphically by the formulæ

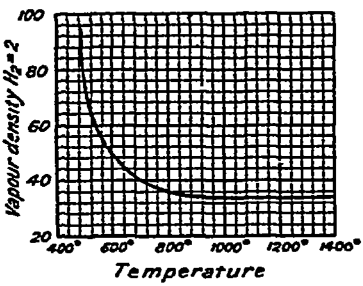


FIG 153 —Vapour Density of Sulphur

```
S=S=S=S          S≡S—S≡S
‖     ‖          |     |
S=S=S=S          S≡S—S≡S
β Sulphur        α Sulphur
```

The former is supposed to represent monoclinic sulphur, and the latter rhombic sulphur The experimental evidence upon which these formulæ are based is very flimsy The molecules of both forms by the freezing and boiling point methods give the same results S_8.

§ 7 Allotropy

The relation between ozone and oxygen and between the different forms of sulphur must be interesting Ozone and oxygen contain but one elemental form of matter This was proved on p 189 The different modifications of sulphur likewise contain but one elemental form of matter This can be proved by showing that a known weight of any of the different forms of sulphur furnish the same amount of sulphur dioxide when burnt in oxygen gas. The experiment can be made by an apparatus resembling that depicted in Fig 154 About 0 1 gram of pure dry sulphur is introduced into

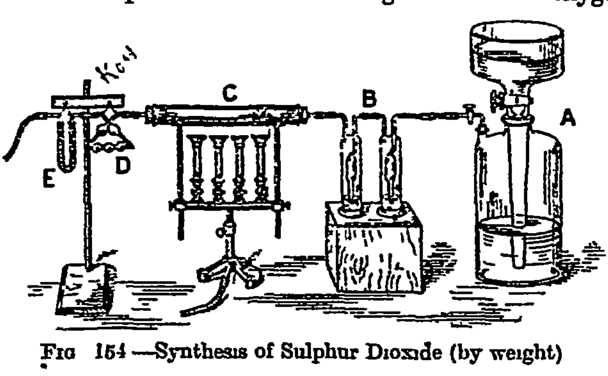


FIG 154 —Synthesis of Sulphur Dioxide (by weight)

a porcelain boat, and all is weighed The boat is introduced into a hard glass tube, *C*, which is connected at one end with a gas holder, *A*, containing oxygen, and wash-bottles, *B*, containing concentrated sulphuric acid to dry the oxygen gas The other end of the combustion tube is connected with weighed glass bulbs, *D*, containing a concentrated solution of potassium hydroxide, and a tube, *E*, containing soda lime in one leg and calcium chloride in the other The current of oxygen is passed through the tube, and the sulphur is very gently heated The sulphur burns, forming sulphur dioxide, which is absorbed by the potash bulbs Take care that the sulphur is all burnt, and that none is left sublimed in the cooler parts of the combustion tube When all the sulphur has been oxidized, the apparatus is disconnected and reweighed The increment in the weight of the potash bulbs represents the sulphur dioxide formed, and the loss in the weight of the porcelain boat, the amount of sulphur consumed This proves that each of the different forms of sulphur is but a modification of one element

A similar phenomenon is presented by many other elements—carbon, phosphorus, selenium, etc That property in virtue of which one element may exist in two or more forms with different properties is called allotropy—from the Greek ἄλλος (allos), another, τρόπος (tropos), shape. One allotropic form is an alias, so to speak, of the other The less common form is sometimes called an "allotrope" or an "allotropic modification" of the other

When a determination can be made of the molecular weight of two allotropic modifications, there is nearly always a difference This is the case, for instance, with oxygen and ozone In consequence, it is often stated that allotropy is due to a difference in the "molecular weight" of the element In other cases, it is assumed that the molecular weights are the same, as is probably the case with some of the different forms of sulphur, but the atoms of the molecule are arranged differently The idea is sometimes expressed in this way "Just as bricks of the same kind in the hands of a builder may be fashioned into various structures, so nature, from the same kind of atoms, builds up molecular structures with widely different properties" The two graphic formulæ for the S_8 sulphur molecule indicated above have been suggested to account for the difference in the two crystalline forms of sulphur The first one has been given to represent the structure of the molecule of β-sulphur, and the second the structure of α-sulphur This, however, is pure hypothesis

Ozone, it will be remembered, is formed by an endothermal reaction The heat absorbed in the production of one molecule of ozone is 34 1 Cals (S Jahn, 1908) Hence we write

$$3O_2 = 2O_3 - 68\ 2 \text{ Cals}, \text{ or } 3O_2 + 68\ 2 \text{ Cals} = 2O_3$$

Accordingly, ozone is supposed to have more available energy than ordinary oxygen Similar remarks might be applied to the different forms of carbon and of phosphorus. In the case of sulphur,

$$\alpha\text{-S} + O_2 = SO_2 + 71\ 08 \text{ Cals.}, \quad \beta\text{-S} + O_2 = SO_2 + 71\ 72 \text{ Cals}$$

This means that the conversion of 32 parts by weight of rhombic sulphur into the monoclinic form is attended by an absorption of 0 64 Cals There is a difference in the energy content of the two forms of

sulphur as was the case with oxygen Hence the definition two allotropic modifications of a substance are composed of one element associated with different proportions of available energy, and consequently they exhibit different physical and chemical properties A definition of this kind describes the facts and no more That is, of course, the function of a good definition But there is a plausible finality about it not altogether pleasing Energy definitions in general are strictly noncommittal and less likely to stimulate the imagination than views such as that which has just been styled "pure hypothesis" This indicates one great objection to the energetic method of dealing with chemical reactions. The atomic, molecular, and kinetic methods are far more likely to prompt new and fruitful investigations

The transition of ordinary α S to β S is reversible There is a definite transition temperature below or above which only one of the forms is stable, and the other form unstable This is a case of enantiotropic allotropy—from the Greek ἐναντιος (enantios), opposite, τροπος (tropos), habit The transformation of λ S to μ S is also reversible, but there is not a definite transition temperature, for the amount of each form present when the system is in equilibrium is determined by the temperature The phenomenon is called dynamic allotropy, to distinguish it from that which precedes In yet a third type of allotropy, the change is irreversible, one form is in a metastable condition at all temperatures This is called monotropic allotropy, to distinguish it from the two phenomena which precede Examples—diamond and graphite, explosive antimony—will be considered later

§ 8 Hydrogen Sulphide—Preparation and Occurrence.

Molecular weight, H_2S = 34 09 Melting point, −86°, boiling point, −62°; critical temperature, +100° Relative vapour density, 34 204 (H_2 = 2), 1 1895 (air = 1) 1000 c c. weigh 1 5392 grams under standard conditions

Occurrence—Hydrogen sulphide occurs in several mineral waters (p 149), in the exhalations from volcanic vents, etc It is also formed during the putrefaction of animal and vegetable matters containing sulphur

Historical—Several references to hydrogen sulphide appear in the writings of the alchemists, where it is described under the general term "sulphurous vapour," and some fetid solutions of the polysulphides, probably containing this gas, were called "divine water"—from the Greek θεῖον (theion), divine or sulphurous K. W Scheele (1777) was the first to investigate the compound systematically

Preparation—Hydrogen and sulphur combine directly when sulphur vapour and hydrogen (or certain hydrocarbons) are passed through a red-hot tube, particularly if the tube be packed with pumice stone or some other similar porous material The gas is best prepared by the action of dilute hydrochloric or sulphuric acid upon ferrous sulphide, FeS, which, in turn, is made by fusing iron and sulphur together (p 19) The reactions are symbolized

$$FeS + H_2SO_4 = FeSO_4 + H_2S\,,\ FeS + 2HCl = FeCl_2 + H_2S$$

Hydrochloric acid is generally preferred to sulphuric acid because the resulting ferrous chloride—$FeCl_2$—is not so liable to crystallize as ferrous sulphate—$FeSO_4$ For small quantities, a similar apparatus to that employed for the preparation of hydrogen is used (Fig 9), and for larger quantities, Kipp's apparatus may be used (Fig 12) Comparatively large quantities of the gas are required intermittently in a testing laboratory,

and scores of different forms of apparatus have been invented for the purpose The gas is generally washed by passing it through a wash-bottle containing water

Ferrous sulphide generally contains a little free iron, and hence some hydrogen will be mixed with the gas For ordinary purposes, this does not matter The gas may also contain traces of hydrocarbons, etc, derived from the action of the acids on the impurities in the iron (A more pure gas is made by heating antimony sulphide with concentrated hydrochloric acid, and washing the gas in water, but calcium, barium, and magnesium sulphides also furnish as pure a gas at the ordinary temperatures $BaS + 2HCl = BaCl_2 + H_2S$ Aluminium sulphide (*q v*) with water gives hydrogen sulphide)

Drying hydrogen sulphide —If the gas is to be dried, phosphoric oxide is used Sulphuric acid should not be used because it is reduced by hydrogen sulphide and free sulphur is deposited $H_2S + H_2SO_4 = SO_2 + 2H_2O + S$ Calcium chloride is often used for drying the gas in spite of the fact that there is a slight decomposition of the calcium chloride $CaCl_2 + H_2S = CaS + 2HCl$

§ 9 Hydrogen Sulphide—Properties and Composition

Hydrogen sulphide is a colourless gas which smells like "ripe" eggs The gas is very poisonous, and it produces headache and vomiting if breathed diluted with air, for a long time According to J Thénard, respiration in an atmosphere containing $\frac{1}{800}$ of its volume of hydrogen sulphide proved fatal to a dog Inhalation of dilute chlorine obtained by wetting chloride of lime with acetic acid is recommended as an antidote

Action of cold —The gas was liquefied by M. Faraday in 1823 by allowing pure ferrous sulphide and pure hydrochloric acid to act upon one another in a stout bent sealed glass tube The gas condenses to a colourless limpid fluid at $+10°$ under a pressure of 15 atmospheres The liquid boils between $-61°$ and $-62°$, and it freezes at $-85°$ Liquid hydrogen sulphide forms a crystalline hydrate when heated with water in a sealed tube The compound, probably $H_2S\,6H_2O$ (R. de Forcrand, 1902), decomposes slowly at ordinary temperatures and pressures, but it may be preserved indefinitely in a sealed tube

Aqueous solutions —Hydrogen sulphide is fairly soluble *in water* 100 volumes of water at 0° dissolve 437 volumes of the gas, and at 20°, 291 volumes The solution is called "hydrogen sulphide water" The solution is supposed to contain H, and HS′, and S″ ions, but the ionization, $H_2S \rightleftharpoons H^{\cdot} + HS'$, is relatively much greater than $H_2S \rightleftharpoons 2H^{\cdot} + S''$, and in a $\frac{1}{10}$ N-aqueous solution only 0 07 per cent of the dissolved hydrogen sulphide is supposed to be ionized The gas can be expelled from the water by boiling Owing to its solubility, the gas should not be collected over cold water, but it is sometimes collected over hot water The aqueous solution decomposes slowly with deposition of sulphur, particularly if exposed to the light—$2H_2S + O_2 = 2H_2O + S$ The aqueous solution has an acid reaction, and it reddens blue *litmus* Hydrogen sulphide reacts with bases forming sulphides When it is desired to emphasize the acid nature of the gas, the aqueous solution is sometimes called hydro-sulphuric acid

Hydrogen sulphide is inflammable in air, and burns with a bluish flame, forming sulphur dioxide and water $2H_2S + 3O_2 = 2SO_2 + 2H_2O$ A mixture of two volumes of hydrogen sulphide with three volumes of oxygen explodes violently when ignited. If the supply of air is limited, free sulphur may be formed $2H_2S + O_2 = 2H_2O + 2S$ A lighted taper dipped into a jar of the gas shows that the gas does not support combustion

Decomposition of hydrogen sulphide —The thermal value of the reaction between hydrogen and sulphur is small

$$H_2 + S_{gas} = H_2S + 4\ 82 \text{ Cals}$$

The gas is easily dissociated by passing it through a hot porcelain tube The dissociation begins about 400°, and it is complete at about 1700° It will be remembered that hydrogen sulphide was formed by passing hydrogen and sulphur vapour through a porcelain tube This means that the reaction belongs to the type of opposing reactions—discussed on p 97 This reaction is symbolized $2H_2S \rightleftharpoons 2H_2 + S_2$ Hydrogen sulphide is also decomposed by passing electric sparks through the gas confined in a tube, Fig 155, over mercury No change in volume occurs, but the decomposition of the gas is evidenced by the deposition of sulphur on the glass in the vicinity of the sparks. There is a considerable local rise of temperature in the vicinity of the sparks, but the gas is immediately cooled as it diffuses into the surrounding gas The products of the reaction do not then have time to react in the converse direction The effect can be compared with a similar result obtained with Deville's "hot and cold tube" (p 193) Decomposition is complete because the sulphur is removed from the zone of the reaction, and deposited as a solid. When hydrogen sulphide is passed through a hot tube, decomposition is not complete, except at very high temperatures, because the sulphur is present in the reacting system as a vapour

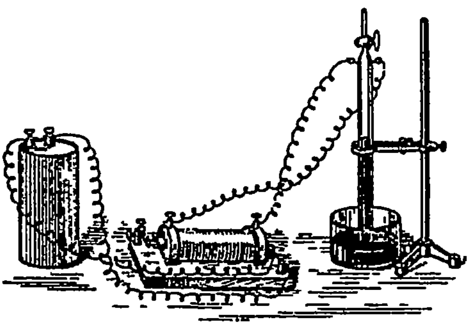


FIG 155 —The Decomposition of Hydrogen Sulphide by Electric Sparks

Reducing action —The relatively small amount of energy absorbed when hydrogen sulphide decomposes corresponds with the fact that it is readily decomposed and the products of decomposition exert a powerful reducing action The action of the gas on sulphuric acid has just been indicated. Hydrogen sulphide reduces moist sulphur dioxide with the separation of sulphur $2H_2S + SO_2 = 2H_2O + 3S$ Fuming nitric acid is reduced with explosive violence This can be shown by dropping acid into a jar of the gas Chlorine, bromine, and fluorine also decompose hydrogen sulphide with the separation of sulphur This can be proved by bringing a jar of chlorine and a jar of hydrogen sulphide mouth to mouth Hydrochloric acid will be formed $H_2S + Cl_2 = S + 2HCl$ A piece of bright silver is very quickly blackened when exposed to the gas owing to the formation of silver sulphide Hydrogen sulphide is often

present in the air of towns, hence silver often tarnishes when exposed to the air of towns The tarnishing of silver by hydrogen sulphide is illustrated by the use of silver spoons with eggs Tin and lead are also quickly tarnished by the gas Some metals decompose hydrogen sulphide very quickly under the influence of heat Tin, lead, and cadmium are examples Sulphides of the metals are formed, and hydrogen gas is liberated $Sn + H_2S = SnS + H_2$

Composition and formula—If a known volume of hydrogen sulphide be heated with metallic tin in a tube over mercury—Fig 156[1]—tin sulphide and free hydrogen equal to the original volume of hydrogen sulphide are formed, similarly, hydrogen sulphide, when decomposed by electric sparks—Fig 155—suffers no change in volume Hence, from Avogadro's hypothesis, it follows at once that one molecule of hydrogen sulphide contains one molecule—two atoms—of hydrogen, and that the formula of hydrogen sulphide is H_2S_n where n has not been determined The specific gravity of hydrogen sulphide (air = 1) is 1 1912, that is, if $H_2 = 2$ be the unit, the relative density of hydrogen sulphide is $1\,1912 \times 28\,755 = 34\,253$ Hence—

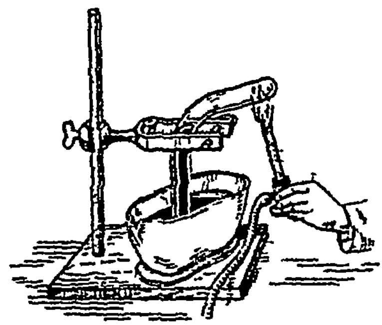


FIG 156—Composition of Hydrogen Sulphide

Molecular weight of hydrogen sulphide	34 204
Weight of hydrogen in the molecule	2 016
Weight of sulphur in the molecule	32 188

This result is sufficiently close to the atomic weight of sulphur—32 07, to prove that there can be one and only one atom of sulphur in the molecule It is therefore concluded that the formula of hydrogen sulphide is H_2S

§ 10 Sulphides.

The *sulphides* can be regarded as salts of hydrosulphuric *acid* even though they are not always prepared directly from hydrogen sulphide. Many sulphides are made by the direct union of sulphur with the metals (p 19) Hydrogen sulphide also forms either sulphides or hydrosulphides with the oxides and hydroxides of the metals, for instance, with lead oxide $PbO + H_2S = PbS + H_2O$, and with lead salts $PbCl_2 + H_2S = PbS + 2HCl$ The lead sulphide is dark brown Hence paints containing lead compounds, when exposed to air contaminated with hydrogen sulphide, are "blackened" Many of the metallic sulphides prepared in this way have characteristic colours, and, in consequence, the colour of the sulphide precipitated when hydrogen sulphide is passed into a solution of salt of the metal, is often strong circumstantial evidence of the presence of particular metals Hydrosulphides are formed by the action of hydrogen sulphide on some of the hydroxides $KOH + H_2S = KSH + H_2O$ The group "SH" resembles the group "OH" in that it is a monad radicle, and forms a group of compounds called hydrosulphides

Polysulphides—Sulphur is fairly soluble in aqueous solutions of the

[1] A slight depression in the tube retains the tin when the mercury is being displaced by the gas while charging the tube

soluble sulphides, *forming a group of polysulphides.* With sodium, for example, a series of sulphides ranging from sodium monosulphide, Na_2S, to the pentasulphide, Na_2S_5, can be obtained The composition and the relations of the polysulphides have not been clearly demonstrated Aqueous solutions of ammonia saturated with hydrogen sulphide mainly consist of ammonium hydrosulphide, NH_4HS (formed $NH_4OH + H_2S = NH_4HS + H_2O$), some ammonium sulphide, $(NH_4)_2S$, and ammonium hydroxide The mixture is often called "ammonium sulphide" When "ammonium sulphide" is allowed to stand, the solution is oxidized, and free sulphur is formed This dissolves in the "ammonium sulphide," forming a polysulphide, $(NH_4)_2S_n$, where *n* may be anything from 1 to 9 The yellow solution—called "yellow ammonium sulphide"—is a reagent much used in analytical work

The alkali sulphides—The sulphides are analogous in many respects with the oxides, and, as with the oxides, we have basic, acidic, and neutral sulphides, as well as persulphides Sulphur is less acidic (electro negative) than oxygen and chlorine, and accordingly, the compounds of sulphur and oxygen and chlorine are not sulphides of oxygen and chlorine, but oxides and chlorides of sulphur Just as the metal sodium decomposes water, H_2O, forming sodium hydroxide, NaOH, so does the metal sodium when heated with *hydrogen sulphide*, H_2S, *form the sulphur analogue of* sodium hydroxide, namely, sodium hydrosulphide, NaSH The same substance is formed when alkaline hydroxide is saturated with a solution of hydrogen sulphide, and, in the case of potassium hydroxide, a crystalline monohydrate, $2KSH.H_2O$, can be isolated from the solution When potassium hydroxide and potassium hydrosulphide are mixed in equivalent proportions, potassium monosulphide and water are formed $KOH + KSH = K_2S + H_2O$ Reddish white prismatic crystals of the pentahydrate, $K_2S.5H_2O$, can be obtained by the evaporation of the aqueous solution in vacuo In the case of sodium, $Na_2S.9H_2O$ is formed The alkaline sulphides are at once hydrolyzed by water $K_2S + H_2O \rightleftharpoons KSH + KOH$ The solution quickly oxidizes on exposure to the air, sulphur is first liberated, and this is dissolved by an alkali sulphide, forming a polysulphide The polysulphide on further oxidation forms a colourless solution of the thiosulphate When potassium carbonate and sulphur are heated together a mixture of variable composition containing sulphate, thiosulphate, and polysulphide is formed The reddish brown product is called "liver of sulphur," or "hepar sulphuris."

Copper sulphides—Cuprous sulphide, Cu_2S, is produced when copper burns in sulphur vapour, when an excess of copper filings is heated with sulphur, and, as a black precipitate, when hydrogen sulphide is passed through solutions of cuprous salts $2CuCl + H_2S = Cu_2S + 2HCl$ The cuprous sulphide is soluble in warm dilute nitric acid, forming copper nitrate and sulphur Cuprous sulphide occurs native in rhombic crystals as *copper glance* A bluish mass of cupric sulphide is formed when copper or cuprous sulphide is heated with sulphur to a temperature below 114°, and as a black precipitate when hydrogen sulphide is passed into solutions of cupric salts The precipitate is inclined to run through filter paper because it is a hydrosol (colloid) The precipitate is coagulated by the addition of dilute hydrochloric acid Cupric sulphide is soluble in hot dilute nitric acid, insoluble in dilute sulphuric acid (cadmium sulphide is soluble

under the same conditions), insoluble in potassium or sodium sulphide, and insoluble in ammonium sulphide It also dissolves in potassium cyanide, forming a complex cyanide from which hydrogen sulphide does not precipitate copper.

Silver sulphide, Ag_2S—Silver sulphide is precipitated by hydrogen sulphide from neutral, acid, or ammoniacal solutions The precipitate is "insoluble" in ammonia, alkaline sulphides, and in dilute potassium cyanide, but it is soluble in concentrated potassium cyanide and in hot dilute nitric acid

Gold sulphide—Hydrogen sulphide precipitates in the cold a black gold disulphide, Au_2S_2 The precipitate is insoluble in dilute acids, readily soluble in *aqua regia*—that is, a mixture of nitric and hydrochloric acids—forming auric chloride Gold disulphide is also soluble in ammonium sulphide, but more readily in potassium sulphide, forming potassium thioaurate, $S{=}Au{-}SK$, from which it is said yellowish-brown gold trisulphide, Au_2S_3, can be precipitated by hydrogen sulphide Metallic gold is precipitated from hot solutions of auric chloride by hydrogen sulphide

Alkaline earth sulphides—The monosulphides are formed by reducing the sulphates with carbon In the case of barium, this reaction is the starting point for the manufacture of the barium salts from barytes, $BaSO_4$ The reaction is symbolized $BaSO_4 + 4C = BaS + 4CO$ Calcium sulphide, CaS, is formed by the action of hydrogen sulphide on heated lime $Ca(OH)_2 + H_2S = 2H_2O + CaS$ The alkaline earth sulphides are white or yellowish-white, and phosphoresce in the dark, after exposure to daylight These sulphides are almost insoluble in water, but like the alkali sulphides, they are hydrolyzed very quickly in boiling water, probably forming hydrosulphide and hydroxide

$Ca{<}^{OH}_{OH}$	$Ca{<}^{SH}_{OH}$	$Ca{<}^{SH}_{SH}$
Calcium hydroxide	Calcium hydroxy hydrosulphide	Calcium hydrosulphide

The hydrosulphides may be obtained in aqueous solution by the action of an excess of hydrogen sulphide on the hydroxide, as indicated above, and crystals of $Ca(SH)_2 6H_2O$ can be obtained from the solution These crystals, when heated in a stream of hydrogen sulphide, give calcium monosulphide, CaS Just as hot alkaline hydrosulphides dissolve sulphur, forming polysulphides, so does boiling milk of lime form calcium polysulphides The sulphides of the alkaline earths—calcium, barium, strontium, and magnesium—can be used as a source of pure hydrogen sulphide, since they decompose with acids giving hydrogen sulphide $CaS + 2HCl = H_2S + CaCl_2$ Calcium sulphide is a by-product in Leblanc's process (*q v*)

The commercial sulphides of the alkaline earths after exposure to light appear luminous when placed in the dark The feeble light emitted by these substances gradually diminishes in intensity, but the property is recovered on exposure to light Calcium sulphide, CaS, was formerly termed "*Canton's phosphorus*," and barium sulphide, BaS, "*Bononian* (*i e* Bolognian) *phosphorus*" These substances are now used in the manufacture of "*luminous paints*" The pure sulphides do not phosphoresce, and the property is therefore dependent on the presence of

some foreign substance Minute traces of other elements, bismuth, cadmium, manganese, zinc, etc, modify the colour of the phosphorescent glow

Zinc sulphide—Zinc sulphide is formed as a white amorphous precipitate when an alkaline sulphide is added to a solution of zinc salt, or when hydrogen sulphide is passed through an alkaline solution of a zinc salt Zinc sulphide is not dissolved by organic acids like acetic and formic acids, but it is soluble in mineral acids evolving hydrogen sulphide Hence zinc sulphide is not precipitated by hydrogen sulphide in acid solutions, cadmium sulphide is precipitated in acid solutions This subject is discussed in the next section **Cadmium sulphide** varies in tint from a bright yellow to an orange red, according to the temperature of precipitation, nature of solution, etc If hydrogen sulphide be passed through a solution of cadmium chloride, the precipitate which forms is an intense orange red colour owing to the formation of **cadmium thiochloride**, Cd_2SCl_2. The reaction is represented $2CdCl_2 + H_2S = 2HCl + Cl{-}Cd{-}S{-}Cd{-}Cl$ The thiochloride passes into the sulphide CdS by the continued action of the hydrogen sulphide, and at the same time, the tint of the precipitate becomes lighter in colour With the chloride, the precipitate never attains the sulphur yellow tint formed when solutions of cadmium nitrate or sulphate are employed Cadmium sulphide is used as a pigment for oil and water colours Cadmium sulphide is insoluble in ammonium sulphide, arsenic, which also forms a bright yellow precipitate, is soluble in ammonium sulphide The fact that zinc oxide dissolves in alkalies while zinc sulphide does not, illustrates the stronger acidic qualities of oxygen in contrast with sulphur

Mercury sulphides—It is said that **mercurous sulphide**, Hg_2S, is produced in the form of brownish black plates by the prolonged action of cold concentrated sulphuric acid on mercury There appears to be some doubt about the existence of mercurous sulphide When hydrogen sulphide acts upon mercurous salts, a mixture of mercuric sulphide and mercury results **Mercuric sulphide**, HgS, is made by rubbing mercury and sulphur together in a mortar It is also formed as a black precipitate by the action of hydrogen sulphide upon a mercuric salt Mercuric sulphide is insoluble in ammonium sulphide and in alkaline hydroxides, but it dissolves in concentrated solutions of alkaline sulphides, more particularly the polysulphides, forming thio salts $HgS + K_2S = Hg(SK)_2$ The thio salt is completely hydrolyzed by water forming red mercuric sulphide $Hg(SK)_2 + H_2O = KOH + KSH + HgS$ When hydrogen sulphide is first passed through the solution of the mercuric salt, a white precipitate is formed. This is supposed to be mercury thiochloride, Cl—Hg—S—Hg—S—Hg—Cl The mercury thiochloride gradually turns brown and then black if the current of gas is continued $Hg_3S_2Cl_2 + H_2S = 3HgS + 2HCl$ The black precipitate is almost insoluble in boiling dilute acids though hot concentrated nitric acid gradually converts it into a white mercury thionitrate, $Hg_3S_2(NO_3)_2$, and finally into soluble mercuric nitrate If the black sulphide be sublimed, a red crystalline sulphide is formed The red crystalline variety of mercuric sulphide is more stable than the black variety When either the black or the red variety is heated, the black compound is formed on cooling, and this may be transformed into the red

variety by merely scratching the surface *Cinnabar*, native sulphide of mercury, HgS, is red

Tin sulphides —When tinfoil is burned in sulphur vapour stannous sulphide, SnS, is formed Stannous hydrosulphide, $Sn(HS)_2$, is precipitated as a brown powder when hydrogen sulphide is passed through a solution of the stannous salt $SnCl_2 + 2H_2S = 2HCl + Sn(SH)_2$ The brown precipitate becomes black and anhydrous on drying The precipitate dissolves in concentrated hydrochloric acid and consequently no tin is precipitated if hydrogen sulphide be passed through a strongly acid solution, on diluting such a solution, however, the stannous sulphide is precipitated Unlike arsenic sulphide, tin sulphide is insoluble in ammonia and ammonium carbonate, and in colourless ammonium sulphide, but it is readily soluble in ammonium and alkaline polysulphides forming thiostannates, *e g* potassium thiostannate, K_2SnS_3, thus $SnS + K_2S + S \rightarrow SSn(SK)_2$ If the solution be acidified, yellow stannic sulphide is precipitated $S{=}Sn{=}(SK)_2 + 2HCl = 2KCl + H_2S + SnS_2$ Stannic sulphide, SnS_2, is precipitated by passing hydrogen sulphide through a (not too acid) solution of a stannic salt, *e g* $SnCl_4 + 2H_2S = 4HCl + SnS_2$ The sulphide is soluble in hydrochloric acid, and hence no precipitation of the sulphide occurs if the solution be strongly acid, such a solution, saturated with hydrogen sulphide, precipitates stannic sulphide when diluted. The yellow stannic sulphide appears to be the anhydride of a thiostannic acid, H_2SnS_3, for it dissolves in alkali sulphides, forming soluble thiostannates as indicated above Stannic sulphide is insoluble in ammonia and ammonium carbonate, and it is converted into the oxide by roasting in air Stannous sulphide alone is prepared in the dry way by heating tin and sulphur together because the heat developed during the reaction converts the stannic sulphide into stannous sulphide and sulphur Stannic sulphide can be made in a dry way by heating tin amalgam, ammonium chloride and sulphur in a retort A complex reaction takes place, resulting in the formation of a mass of yellow scales called "mosaic gold," and this is used as a pigment "Mosaic gold" is not attacked by alkaline sulphides nor by nitric acid, it is attacked by *aqua regia*, forming stannic chloride and sulphur The insoluble sulphides of tin are most readily obtained in a soluble condition by fusing them together with sodium carbonate and sulphur, and extracting the resulting sodium thiostannate with water.

Lead sulphide, PbS —Lead sulphide occurs in nature as galena in well-formed cubic crystals with a lustre resembling metallic lead (Lead sulphide is formed by reducing the sulphate with carbon, by heating lead in sulphur vapour, and as a black precipitate by passing hydrogen sulphide through neutral, acid, or alkaline solutions of a lead salt.) If hydrochloric acid be present, an orange, yellow, or red precipitate of lead thiochloride, Pb_2SCl_2, may be formed

$$2Pb{<}^{Cl}_{Cl} + {}^{H}_{H}{>}S = 2HCl + S{<}^{Pb-Cl}_{Pb-Cl}$$

This is immediately decomposed by more hydrogen sulphide, forming a black lead sulphide Boiling dilute nitric acid dissolves lead sulphide, forming lead nitrate with the separation of sulphur Concentrated nitric acid oxidizes it to lead sulphate Unlike tin sulphide, lead sulphide is insoluble in alkaline hydroxides and sulphides Lead sulphide melts just over 930°, and sublimes in vacuo or in a current of an inert gas, forming

small cubic crystals. Heated with free access of air, it forms lead sulphate

Aluminium sulphide, Al_2S_3.—Aluminium sulphide can be prepared as a greyish black solid by heating finely divided aluminium with iron pyrites $4Al + 3FeS_2 = 2Al_2S_3 + 3Fe$, it is also formed when sulphur is thrown upon strongly heated aluminium Aluminium sulphide is decomposed by water with the evolution of hydrogen sulphide $Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S$ Atmospheric moisture also decomposes the sulphide in a similar manner The sulphides of aluminium and of chromium cannot be prepared in the presence of water, hence when ammonium sulphide is added to solutions of chromium or aluminium salts, the hydroxides, not the sulphides, are precipitated The hydrosulphide is probably formed first $AlCl_3 + 3NH_4HS = 3NH_4Cl + Al(SH)_3$, and this is at once hydrolyzed $Al(SH)_3 + 3H_2O = Al(OH)_3 + 3H_2S$

Iron sulphides.—By projecting a mixture of iron filings and sulphur into a red hot crucible, a fused mass of ferrous sulphide, FeS, is formed. A little black ferrous sulphide is precipitated when hydrogen sulphide is passed through neutral solutions of ferrous salts, if an alkaline acetate be present, a little more ferrous sulphide is precipitated, but the precipitation is not complete, alkali and ammonium sulphide precipitate black ferrous sulphide $FeCl_2 + (NH_4)_2S = 2NH_4Cl + FeS$ The precipitate is readily soluble in dilute acids, even acetic acid, with the evolution of hydrogen sulphide Moist ferrous sulphide is readily oxidized when exposed to the air, forming first a brownish basic sulphate with the separation of sulphur Hydrogen sulphide and ammonium sulphide readily reduce ferric to ferrous salts with the separation of sulphur $2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$, and the ferrous chloride then behaves as indicated above Hence ferric sulphide, Fe_2S_3, cannot be made by precipitation with hydrogen sulphide, but it can be made by fusing equal weights of iron and sulphur at about 550°, and by passing a current of hydrogen sulphide over ferric oxide heated to about 100°

Ferrous sulphide is comparatively rare in nature, while iron pyrites, FeS_2, is exceedingly common. The latter can be made artificially by gently heating iron with an excess of sulphur at a low red heat. Iron pyrites occurs in two forms, one, pyrite, has a specific gravity about 5 1 It crystallizes in the cubic system, is but very slowly oxidized in air, the other, marcasite, has a specific gravity about 4 8, crystallizes in the rhombic system, is less stable than pyrite, and is oxidized comparatively quickly in air, and on this account marcasite has been largely used in the manufacture of "copperas," ferrous sulphate The former has been prepared artificially, the latter has not. Pyrite is not acted upon by dilute acids, but hot concentrated hydrochloric acid decomposes it, forming hydrogen sulphide and sulphur If heated in hydrogen, sulphur is evolved and ferrous sulphide remains When heated in air, pyrites and many other sulphides of iron produce ferric oxide and sulphur dioxide This action is partly due to the stronger acidic properties of oxygen over sulphur, and also to the volatility of sulphur dioxide which removes sulphur from the zone of the reaction Many sulphides, *e.g* lead sulphides, form sulphates when heated in air *Magnetic iron pyrites*, or ferrosoferric sulphide also called *pyrrholine*, or *pyrrhotite*, supposed to be in the ideal case Fe_3S_4 is the sulphur analogue of magnetic oxide of iron, Fe_3O_4 The

ratio Fe S varies a great deal in native specimens, their composition is said to "range from Fe_5S_6 to $Fe_{16}S_{17}$, chiefly $Fe_{11}S_{12}$" This is taken to mean that the minerals are probably mixtures of different sulphides, and may be of sulphur, etc.

§ 11 The Action of Hydrogen Sulphide on Metallic Salt Solutions.

Hydrogen sulphide is a valuable reagent Its reactions with the different metallic salts enable the metals to be separated into groups as a preliminary to more detailed examination Thus—

I Sulphides insoluble in dilute acids

(a) Soluble in alkaline sulphides—arsenic, antimony, stannic, gold, and platinum sulphides

(b) Insoluble in alkaline sulphides—mercury, silver, lead, copper, bismuth, cadmium, and stannous sulphides

II Sulphides soluble in dilute mineral acids but insoluble in the presence of alkalies—iron, cobalt, nickel, manganese, and zinc sulphides

III Sulphides not precipitated by hydrogen sulphide—chromium, aluminium, magnesium, barium, strontium, calcium, potassium, and sodium Chromium and aluminium are precipitated as hydroxides

The method of classifying certain elements into groups—those which form soluble and those which form insoluble sulphides in hydrochloric acid—frequently conveys wrong ideas of the properties of the sulphides The solubility of the sulphides depends upon the concentration of the acid For instance, if hydrogen sulphide be passed into 5 c c of a solution of 2 grams of tartar emetic—potassium antimonyl tartrate—in 15 c c of hydrochloric acid (sp gr 1 175) and 85 c c of water, antimony sulphide will be precipitated, but not if 15 c c of hydrochloric acid had been employed without the water In one case, $2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl$, and in the second case, $Sb_2S_3 + 6HCl = 3H_2S + 2SbCl_3$ In other words, the antimony sulphide, in the second case, is decomposed by the acid as fast as it is formed Similarly, no lead will be precipitated by hydrogen sulphide from a solution containing 3 per cent of hydrochloric acid, HCl, and if the solution has 2 5 per cent of acid, the lead sulphide will be imperfectly precipitated—*i e* part will be precipitated, and part will be decomposed as fast as it is formed Similarly, a 5 per cent boiling solution of hydrochloric acid will prevent the precipitation of cadmium sulphide.

If a metallic sulphide, MS, be treated with hydrochloric acid, hydrogen sulphide and a metallic chloride will be formed $MS + 2HCl = MCl_2 + H_2S$ Conversely, when a metallic chloride in aqueous solution is treated with hydrogen sulphide, the metallic sulphide and hydrochloric acid will be produced $MCl_2 + H_2S = MS + 2HCl$ Hydrochloric acid thus accumulates in the solution as the action goes on If any more sulphide be produced, after the hydrochloric acid has attained a certain limiting concentration, the excess of sulphide will be at once decomposed by the acid There are then two simultaneous opposing reactions (1) Formation of the metallic sulphide and hydrochloric acid, and (2) formation of chloride and hydrogen sulphide In illustration, if a current of hydrogen sulphide be passed through a saturated solution of zinc chloride, part of the metal

is precipitated, but when the hydrochloric acid has attained a certain concentration, the action apparently ceases because the reverse change sets in Hence the precipitation will be incomplete In illustration, take the case of lead chloride

$$PbCl_2 + H_2S \rightleftharpoons PbS + 2HCl$$

When equilibrium is established, the solution contains lead chloride, hydrogen sulphide, and hydrogen chloride Using symbols in square brackets to represent the concentrations (gram molecules per litre) of the respective compounds in the solution, it follows from the equilibrium law, that

$$\frac{[PbCl_2] \times [H_2S]}{[HCl]^2} = \text{Constant}$$

This shows that if the concentration of the acid be increased, and the concentration of the hydrogen sulphide be constant, the amount of lead chloride which remains in solutions (that is, escapes precipitation) will increase in order to keep the numerical value of the "constant" always the same Conversely, if it be desired to keep the amount of lead chloride in the solution as low as possible, it is necessary to keep the concentration of the acid down to a minimum value A certain amount of acid is usually required to keep other metals in solution, zinc, for example.

The concentration of the hydrogen sulphide in the solution is practically constant (0 0073 gram molecules per litre at 20°) when the gas is passing through the solution If the concentration of the hydrogen sulphide were large and the concentration of the metallic chloride small, a very large excess of acid would be needed to prevent metal being precipitated by the hydrogen sulphide. It will be observed, however, that the concentration of the hydrogen sulphide under ordinary circumstances is small In consequence, a comparatively small amount of acid suffices to prevent the separation of sulphides of zinc, iron, nickel, cobalt, manganese If the solubility of the hydrogen sulphide had been greater than it is, some of the metals—zinc, iron, nickel . would have been included in the "hydrogen sulphide group", and conversely, had the solubility of hydrogen sulphide been less than it is, some of the present members of the "hydrogen sulphide group" would not have been there For instance, tin, lead, cadmium

Under ordinary conditions, the solubilities of the sulphides in hydrochloric acid, starting with the least soluble, are approximately in the order

As, Hg, Cu, Sb, Bi, Sn(ic), Cd, Pb, Sn(ous), Zn, Fe, Ni, Co, Mn

Elements wide apart in the list can be easily separated by hydrogen sulphide in acid solutions, but elements close together in the list require a very careful adjustment of the amount of acid in solution before satisfactory separations can be made For instance, the separation of cadmium or lead from zinc by means of hydrogen sulphide is only satisfactory when the concentration of the acid is very carefully adjusted If too much acid be present, cadmium or lead will be imperfectly precipitated, while if too little acid be present, zinc will be precipitated with the cadmium or lead. Hence there is no sharp line of demarcation between metals precipitated and metals not precipitated by hydrogen sulphide from acid

solutions All depends upon the concentration of the acid This is arbitrarily adjusted so that antimony, arsenic, lead, bismuth, cadmium, copper, mercury, and tin are precipitated by making the volume of the solution such that it contains approximately 10 c c of hydrochloric acid (sp gr 1 12) per 100 c c before passing the hydrogen sulphide The aluminium, iron, zinc, nickel, cobalt, and manganese salts will be found in the filtrate Barium, strontium, calcium, and magnesium salts will also be found in the filtrate along with the alkalies, because the sulphides of these elements are attacked and decomposed by water and by acids *E g* $Ca_2S + 2H_2O \rightleftharpoons Ca(OH)_2 + Ca(SH)_2$

The above remarks can easily be translated into the language of ions The precipitation is then supposed to proceed according to the equation $M^{\cdot\cdot} + 2H_2S \rightleftharpoons M(HS)_2 + 2H^{\cdot}$, or $M^{\cdot\cdot} + H_2S \rightleftharpoons MS + 2H^{\cdot}$ That is, the bivalent ion $M^{\cdot\cdot}$ reacts with the hydrogen sulphide, forming the sparingly soluble MS, or $M(HS)_2$, which precipitates In the process, hydrogen (acid) ions, $H^{\cdot}$, are formed The hydrogen sulphide is itself supposed to be ionized in aqueous solution as indicated above $H_2S \rightleftharpoons H^{\cdot} + HS' \rightleftharpoons 2H^{\cdot} + S''$ The metal chloride, say, is also ionized $MCl_2 = M^{\cdot\cdot} + 2Cl'$ Hence the solution may be supposed to contain $MCl_2 + H_2S \rightleftharpoons M^{\cdot\cdot} + 2Cl' + S'' + 2H^{\cdot}$ When the solubility product $[M^{\cdot\cdot}] \times [S'']$ is exceeded, the solid MS separates from the solution, leaving hydrochloric acid ions behind $2H^{\cdot} + 2Cl'$ A further amplification on the lines indicated in the text can now be made Here, as elsewhere, it makes very little difference which mode of expression be used The facts will stand for ever, and they are independent of fashion, taste, or caprice, the language used in describing the facts, like other customs, changes according to the prevailing or fashionable hypothesis

§ 12 Hydrogen Persulphide, or Hydrogen Disulphide.

If dilute hydrochloric acid be poured into a solution of sodium polysulphide, say, Na_2S_5, milk of sulphur is precipitated (p 401) $Na_2S_5 + 2HCl = 2NaCl + H_2S + 4S$ On the contrary, if the polysulphide be poured into the acid, little or no hydrogen sulphide is evolved, and a yellow oily liquid is obtained This was once considered to be a mixture of hydrogen pentasulphide, H_2S_5, with other hydrogen polysulphides When the oil is distilled under reduced pressure, the fraction which is obtained at 69° under a pressure of 2 mm of mercury is a pale yellow oil with a molecular weight, by the freezing point method, corresponding with H_2S_3—hydrogen trisulphide The fraction which distils at 74°–75°, under atmospheric pressure, has the composition H_2S_2 This is hydrogen disulphide or hydrogen persulphide The persulphide dissolves in benzene, forming a clear solution Hydrogen persulphide is a colourless oily liquid with a specific gravity 1 376 It has a pungent irritating smell, and decomposes gradually into hydrogen sulphide and sulphur The decomposition is faster in presence of water, and particularly alkalies Mere contact with glass, paper, dust, etc., induces rapid decomposition Hydrogen persulphide burns with a blue flame Like its analogue, hydrogen peroxide, it has oxidizing and reducing qualities.

Hydrogen trisulphide, H_2S_3, prepared as just described, resembles the

persulphide in many of its properties, but its specific gravity is 1·496, and it solidifies between $-52°$ and $-54°$. The three hydrogen sulphides—H_2S, H_2S_2, and H_2S_3—are all the hydrogen polysulphides whose individuality has been clearly demonstrated, although a whole series ranging from H_2S_5 to H_2S_9 has been reported. There is a certain analogy between H_2O and H_2S, and between H_2O_2 and H_2S_2. The hydrosulphides are particularly interesting, for they bring out the peculiar property of sulphur atoms to form chains in which hydrogen can be replaced by an SH group:

$S<^{H}_{H}$	$S<^{SH}_{H}$	$S<^{SH}_{SH}$	$S<^{S-SH}_{SH}$	$S<^{S-SH}_{S-SH}$
Hydrogen monosulphide	Hydrogen disulphide	Hydrogen trisulphide.	Not known	Hydrogen pentasulphide

These are sometimes called chain formulæ; the pentasulphide, for example, is virtually H—S—S—S—S—S—H. This is D. I. Mendeléeff's method of representing the constitution of the hydrogen sulphides. Several other schemes have been proposed, but no decisive evidence is available to justify one in preference to another. I. Bloch and F. Hohn (1908), indeed, *assume* that two or even three isomeric modifications may exist in equilibrium, side by side, at any given temperature:

$$S{=}S<^{H}_{H} \rightleftharpoons H{-}S{-}S{-}H, \quad S{=}S{=}S<^{H}_{H} \rightleftharpoons S{=}S<^{H}_{SH} \rightleftharpoons H{-}S{-}S{-}S{-}H$$

Hydrogen persulphide — Hydrogen trisulphide

It is assumed that at low temperatures Mendeléeff's chain type of molecules predominates; and at higher temperatures, when the colour darkens, that the more condensed type of molecules prevails.

§ 13 Sulphur Chlorides

The study of the sulphur chlorides throws an interesting light on the valency of sulphur, and also on the constitution of some other sulphur compounds.

Sulphur chloride.—When dry chlorine is passed into sulphur heated in a retort, *A*, Fig. 157, the two elements combine directly, forming sulphur chloride—S_2Cl_2—which collects in the receiver *B*, cooled by a current of cold water, as a yellow liquid. The oil is purified by redistillation. The pale yellow liquid when pure has a pungent smell. It boils between 138° and 140°. The liquid fumes in moist air and is decomposed by water, forming sulphur dioxide, hydrochloric acid, and sulphur: $2S_2Cl_2 + 3H_2O = 4HCl + H_2SO_3 + 3S$. Sulphur chloride is used as a solvent for sulphur in the manufacture of rubber goods. Its vapour density is 13·5 ($H_2=1$), corresponding with the molecule S_2Cl_2, not SCl. Hence "sulphur monochloride" does not appear a very appropriate name for this compound.

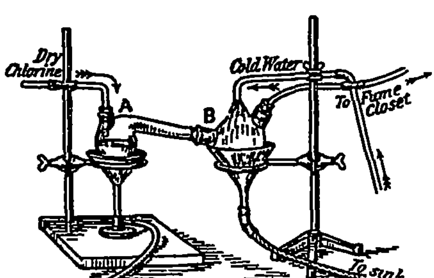
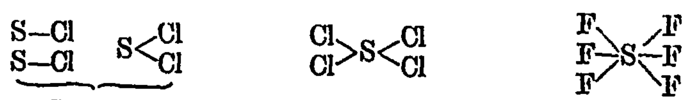


FIG. 157.—Preparation of Sulphur Chloride—S_2Cl_2.

Sulphur dichloride.—If chlorine be passed into sulphur chloride, cooled in ice, a garnet-red liquid, said to be SCl_2, is obtained $S_2Cl_2 + Cl_2 = 2SCl_2$. A mixture of liquid chlorine and sulphur chloride, S_2Cl_2, in a sealed tube, at about 15°, gradually passes into a similar product The molecular weight by the freezing point method in xylene, bromine, acetic acid, etc, corresponds with the molecule SCl_2 It freezes at $-80°$, and it can be distilled with but little decomposition under reduced pressures

Sulphur tetrachloride.—If the temperature be still further reduced to $-22°$, still more chlorine is taken up by sulphur chloride, and sulphur tetrachloride, SCl_4, is formed $S_2Cl_2 + 3Cl_2 = 2SCl_4$ The red liquid begins to decompose into sulphur dichloride and chlorine directly it is removed from the freezing mixture at $-22°$ It freezes to a yellowish white solid between $-30°$ and $-31°$ Sulphur tetrachloride unites with gold chloride and with stannic chloride, molecule for molecule, forming double compounds, *e g* $SnCl_4 \cdot SCl_4$

Bromine forms sulphur bromide, S_2Br_2, when heated with bromine, but the existence of sulphur iodide is doubtful, because the product prepared by the evaporation of a mixed solution in carbon disulphide, though sold commercially as sulphur iodide, is considered to be a mixture or a solid solution. H Moissan has isolated a sulphur hexafluoride—SF_6—which is formed by the action of fluorine upon sulphur The gas solidifies at $-55°$, and the liquid boils a few degrees higher The gas is comparatively stable and inert chemically These compounds of sulphur are interesting from the point of view of the valency hypothesis Here is strong presumptive evidence of the variable valency of sulphur, and almost conclusive evidence that sulphur can be sexivalent



S dyad S tetrad S hexad

It might be supposed that the properties of the sulphur fluorides would be analogous with those of the chlorides, but the resemblances are not very close The fluorides are more stable than the chlorides

Questions.

1 Describe the preparation of dry sulphuretted hydrogen from ferrous sulphide and outline experiments by which (*a*) hydrogen, (*b*) sulphur can be separated from it Explain carefully why the molecular formula H_2S is assigned to sulphuretted hydrogen —*Sheffield Univ*

2 Give an account of the occurrence of the element of sulphur, and its compounds in nature Describe the preparation and properties of the various modifications of sulphur —*St Andrews Univ*

3 Explain fully the meaning of the symbolic equation $FeS + 2HCl = FeCl_2 + H_2S$ If 6 8 grams of ferrous sulphide are taken, what would be the weight obtained of each of the substances on the right-hand side of the equation (Atomic weight of iron = 56, sulphur 32, chlorine 35½) —*Oxford Junior Locals*

4 What do you know regarding the general behaviour of metallic sulphides towards (*a*) water, (*b*) hydrochloric acid, (*c*) caustic soda? Give equations —*St Andrews Univ*

5 You are required to convert a given weight of sulphur into hydrogen sulphide as completely as possible How would you proceed? What are the reactions of gaseous hydrogen sulphide respectively with (*a*) gaseous ammonia, (*b*) aqueous sodium hydroxide, (*c*) aqueous copper sulphate, and (*d*) gaseous sulphur dioxide?—*Univ North Wales*

CHAPTER XXIII

Compounds of Sulphur with Oxygen

§ 1 Sulphur Dioxide—Occurrence and Preparation

Molecular weight, $SO_2 = 64.07$ Melting point, $-73°$; boiling point, $-8°$ Relative density ($H_2 = 2$), 64.05, (air = 1) 2.264

Occurrence.—Sulphur dioxide is found among the fumes from volcanic vents, in the springs of volcanic districts, and in the air of towns where it is derived from the sulphur compounds in the coal

History.—The use of sulphur for disinfecting purposes has been known from very early times. It is referred to in Homer where Odysseus, after the slaughter of the suitors, and probably recognizing the need for a general cleansing, calls

> Quickly, O Nurse, bring fire that I may burn
> Sulphur, the cure of ills

J Priestley (1770) prepared the gas by the action of hot concentrated sulphuric acid on mercury Priestley called it sulphurous acid

Preparation.—Sulphur dioxide is formed when sulphur burns in air $S + O_2 = SO_2$ Between 6 and 8 per cent of the sulphur is simultaneously oxidized to sulphur trioxide, SO_3 If the sulphur be burnt in oxygen gas between 2 and 3 per cent burns to sulphur trioxide[1] The nitrogen in the air seems to favour the production of sulphur trioxide, whereas moisture and carbon dioxide do not affect the result appreciably When sulphur is oxidized by a peroxide—*e.g* manganese peroxide—sulphur dioxide is formed $MnO_2 + 2S = MnS + SO_2$ Sulphur dioxide is also formed when the sulphides of some metals are roasted in air—*e.g* iron or copper pyrites $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$ This reaction is very commonly used for making the sulphur dioxide employed in the manufacture of sulphuric acid

The most convenient laboratory process, for small quantities, is to decompose commercial sodium bisulphite with concentrated sulphuric acid A concentrated—40 per cent.—solution of sodium bisulphite, $NaHSO_3$, is placed in a flask, which is then fitted with a tap funnel containing concentrated sulphuric acid, as indicated in Fig 47 The gas can be washed by passing it through concentrated sulphuric acid The reaction is symbolized $NaHSO_3 + H_2SO_4 = NaHSO_4 + H_2O + SO_2$. The same gas is made by reducing sulphuric acid with charcoal, sulphur, silver, copper

[1] The presence of sulphur trioxide in the sulphur dioxide formed when sulphur burns in air accounts for the "foggy" appearance of the gas This will be understood when the properties of the trioxide have been studied

or mercury The charcoal process is used on a manufacturing scale when the presence of carbon dioxide, a by-product of the reaction, is not detrimental, for instance, in the manufacture of sulphites The reaction is represented $C + 2H_2SO_4 = 2H_2O + CO_2 + 2SO_2$ When sulphur is the reducing agent, the sulphur is simultaneously oxidized to sulphur dioxide $S + 2H_2SO_4 = 2H_2O + 3SO_2$ In practice, the action is slow because the sulphur melts and offers but a small surface to the action of the acid Copper and sulphuric acid are often employed in the laboratory when the bisulphite process is not convenient Half fill a flask with copper turnings, and add sufficient sulphuric acid to not quite cover all the copper The gas comes off when the flask is gently warmed The apparatus is illustrated in Fig 94, where two washing-bottles containing concentrated sulphuric acid are shown attached to the delivery tube in order to dry the gas

The reaction is somewhat complex It is usually symbolized $Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$ It is possible that the first action resembles the effect of zinc on dilute sulphuric acid whereby hydrogen is developed $Cu + H_2SO_4 = CuSO_4 + H_2$ The hydrogen reduces the sulphuric acid to sulphur dioxide $H_2 + H_2SO_4 = 2H_2O + SO_2$ In confirmation of this view hot concentrated sulphuric acid is reduced to sulphur dioxide by passing hydrogen through the liquid Some of the sulphuric acid is possibly reduced to hydrogen sulphide At any rate, cuprous sulphide, Cu_2S, and cuprous sulphate, Cu_2SO_4, will be found associated with the copper sulphate in the flask.

§ 2 The Properties of Sulphur Dioxide

Sulphur dioxide is a colourless gas with a smell characteristic of burning sulphur Sulphur dioxide is an acute blood poison According to Ogata (1884) 0 04 per cent in air causes a difficulty in breathing after a few hours Sulphur dioxide is also injurious to vegetation, and it is one of the "*noxious vapours*" complained about in manufacturing districts

Aqueous solutions —The gas is more than twice as heavy as air, and in consequence, it can be collected by the upward displacement of air The gas cannot be collected satisfactorily over water because it is easily soluble in that menstruum One volume of water at 0° dissolves 79 8 volumes of sulphur dioxide, and at 20°, 38 4 volumes The aqueous solution is strongly acid, and it has the general properties characteristic of acids It is hence called sulphurous acid, and is represented by the formula H_2SO_3 The gas itself is accordingly called sulphurous anhydride The dissolved gas is all expelled on boiling the aqueous solution The existence of the compound H_2SO_3 is inferred from analogy with other acids, and from the general behaviour of aqueous solutions of the gas. The solution probably contains both dissolved sulphur dioxide and sulphurous acid At 0° a crystalline hydrate—SO_2 $6H_2O$, or H_2SO_3 $5H_2O$—is obtained, but several other crystalline hydrates have been reported The aqueous solution readily decomposes into sulphuric acid and free sulphur when exposed to light $3H_2SO_3 = S + 2H_2SO_4 + H_2O$

The action of cold —The gas is easily liquefied A pressure of 1 5 atmospheres suffice, for the condensation of the gas at 0°, and at −10° the gas liquefies under ordinary pressures It is therefore sufficient to

thoroughly dry the gas obtained by the action of copper on sulphuric acid by passing the gas through a couple of wash bottles as indicated in Fig 94, and then lead the gas through a condensing tube, Fig 158, immersed in a freezing mixture the freezing mixture is omitted in the drawing The gas condenses to a clear, colourless, transparent, limpid liquid which boils at $-8°$ and solidifies at $-70°$ to a white snowlike mass Liquid sulphur dioxide is sold commercially in thick glass "syphons," and where available, the "syphons" are used as a source of sulphur dioxide for laboratory work By the evaporation of liquid sulphur dioxide a temperature approaching $-50°$ can be obtained Hence like ammonia and carbon dioxide, sulphur dioxide is used as a refrigerating agent Liquid sulphur dioxide is a good solvent for phosphorus, iodine, sulphur, resins, etc The conductivity of these solutions is sometimes greater than that of aqueous solutions

Dissociation of sulphur dioxide—When the gas is passed through Deville's "hot and cold tube," Fig 77, the surface of the silver tube is blackened owing to the formation of silver sulphide, at the same time, sulphur trioxide can be detected in the products of the reaction Dry sulphur dioxide dissociates appreciably at 1200°, into sulphur and sulphur trioxide $3SO_2 \rightleftharpoons S + 2SO_3$, *and the moist gas into sulphur and sulphuric acid* H_2SO_4 Like hydrogen sulphide, sulphur dioxide is decomposed by a series of electric sparks with the deposition of sulphur on the glass in the vicinity of the sparks. The reaction appears to be $3SO_2 \rightleftharpoons S + 2SO_3$ If a beam of light be sent through a long cylinder of the gas, at first, the gas appears to be clear and transparent, but in a few minutes the gas appears to decompose, for misty wavering striæ appear, and gradually the whole tube appears to be filled with a fog This action of light in certain gases is sometimes called **Tyndall's effect.** In the present case the effect appears to be due to the decomposition of the sulphur dioxide, probably $3SO_2 = 2SO_3 + S$ If left a short time in the dark the gas becomes clear owing to the recombination of the sulphur and sulphur trioxide

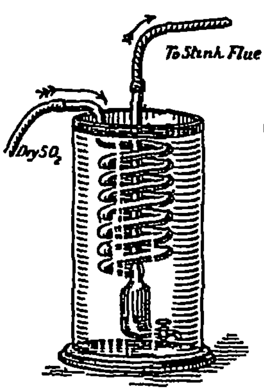


FIG 158—Gas Condensing Tube

Oxidizing properties—Sulphur dioxide is incombustible and a non supporter of ordinary combustion Some substances are able to burn in the gas by abstracting its oxygen In this way, sulphur dioxide appears to act as an oxidizing agent Ignited magnesium ribbon, for instance, continues to burn in the sulphur dioxide Finely divided iron when heated in a stream of sulphur dioxide forms a mixture of iron oxide and sulphide with incandescence Sulphur is deposited when hydrogen sulphide and sulphur dioxide are brought into contact, say by placing a jar of sulphur dioxide and of hydrogen sulphide mouth to mouth The gaseous exhalations from some volcanoes contain these two gases which, on mingling together, mutually decompose with the formation of sulphur (p 393) $2H_2S + SO_2 = 2H_2O + 3S$ This reaction does not occur if the gases are thoroughly dried

Composition of sulphur dioxide—When sulphur burns in oxygen, no change in volume occurs when the gas is cooled. The apparatus, shown

in Fig 156 or Fig 230 can be used Taken in conjunction with Avogadro's hypothesis, the experiment proves that sulphur dioxide contains its own volume of oxygen. That is to say, one molecule of sulphur dioxide contains two atoms of oxygen, and the formula of sulphur dioxide is S_nO_2, where n is to be determined Again, the relative density of sulphur dioxide is 64 046 ($H_2 = 2$) Hence

One gram-molecule of sulphur dioxide weighs	64 05
One gram-molecule of oxygen weighs	32 00
Weight of sulphur in the molecule	32 05

The number 32 05 can represent one and only one atom of sulphur if 32 07 be the atomic weight of sulphur, since the two numbers are nearly the same.

The salts of sulphurous acid—Two series of salts, exemplified by $KHSO_3$ and K_2SO_3 are known, the former are the acid sulphites or the bisulphites, and the latter the normal sulphites Hence sulphurous acid is dibasic With the exception of the alkaline salts, most of the sulphites are sparingly soluble in water The alkaline sulphites are alkaline to litmus If the sulphites are treated with strong acids, the anhydride, SO_2, is evolved as indicated in one of the methods of preparation. The sulphites decompose on heating with the formation of sulphates. *e g* $4Na_2SO_3 \rightarrow 3Na_2SO_4 + Na_2S$, the bisulphites first lose H_2SO_3 before decomposing in this way $2NaHSO_3 \rightarrow Na_2SO_3 + H_2SO_3$ The sulphites, as well as sulphurous acid itself, are readily oxidized The presence of glycerine or sugar retards the rate of oxidation, possibly because the more viscid solutions offer some resistance to the free circulation of oxygen in the fluid. The monobasic acids $HRSO_3$—where R is a radicle CH_3, C_6H_5, etc —are called sulphonic acids

Reducing properties of sulphur dioxide—Sulphur dioxide is a powerful reducing agent It reduces permanganates to manganous salts, chromates to chromic salts, ferric to ferrous salts, etc The latter reaction is often used in analytical work for the reduction of iron previous to its determination by volumetric processes

The bleaching effects of sulphurous acid are due to its reducing properties Moistened red rose-leaves, or fabrics dyed with, say, "magenta" dye, when placed in the gas lose their colour The sulphur dioxide appears to react with the colouring matter, forming sulphuric acid and hydrogen $SO_2 + 2H_2O = H_2SO_4 + H_2$ This idea is supported by the fact that the colour of many articles bleached by sulphur dioxide can be restored by exposing the article to oxidizing conditions The familiar yellow colour which gradually comes to bleached sponges, flannels, etc, is an example The colour of bleached rose leaves gradually returns when the rose-leaves are exposed to the air, or when the bleached leaves are dipped in dilute sulphuric acid This shows that the colouring agent is not really destroyed during the bleaching

An aqueous solution of sulphur dioxide reduces chlorine, forming hydrochloric and sulphuric acids $SO_2 + 2H_2O + Cl_2 = 2HCl + H_2SO_4$ Hence sulphurous acid is used as an "anti-chlor," that is, as an agent to remove the last traces of chlorine from articles bleached with chlorine The goods are dipped in a solution of sulphur dioxide, or a sulphite The extended use of the term reduction might here be emphasized A reducing agent is a substance which can (1) remove oxygen from other substances, (2) decrease the non-metallic part of a compound, *e g* $SnCl_4 \rightarrow SnCl_2$,

(3) add hydrogen to an element or compound, *e g* $Cl \rightarrow HCl$ The definition of an oxidizing agent—oxidation—can also be extended in the converse manner

When sulphur dioxide is passed over lead peroxide, the reaction, $PbO_2 + SO_2 = PbSO_4$, occurs, and the mass glows brightly The sulphur dioxide here reduces the peroxide, so also sodium peroxide, when "dusted" into a cylinder of the gas, glows brightly owing to the heat evolved during the reaction $Na_2O_2 + SO_2 = Na_2SO_4$

Action on hydrogen iodide—Sulphur dioxide reduces iodine to hydrogen iodide, HI, in the presence of water $SO_2 + 2H_2O + I_2 = 2HI + H_2SO_4$ The reaction stops when a certain amount of hydrogen iodide has been formed. Again, concentrated solutions of hydrogen iodide are oxidized by sulphuric acid, and the latter is reduced to sulphur dioxide $H_2SO_4 + 2HI = I_2 + 2H_2O + SO_2$ This reaction is the reverse of that which immediately precedes The two opposing reactions are in equilibrium when the speeds of the direct and reverse changes are equal In other words, this reaction belongs to the type indicated on p 97, and should be symbolized $I_2 + SO_2 + 2H_2O \rightleftharpoons H_2SO_4 + 2HI$ This reaction is important because the amount of sulphurous acid or of its salts in a given solution can be determined by adding a solution of iodine of known strength from a burette until the iodine solution is no longer decolorized. The equation furnishes the necessary data for the calculation Every 253 84 grams of iodine corresponds with 64 07 grams of sulphur dioxide The amount of sulphur dioxide must not exceed 0 05 per cent or the "back reaction" will appreciably affect the results

Action on iodic acid.—The reduction of iodic acid, HIO_3, or of an iodate by contact with sulphur dioxide, results in the formation of sulphuric acid, and in the liberation of iodine $2HIO_3 + 4H_2O + 5SO_2 = 5H_2SO_4 + I_2$ Strips of paper dipped in a solution of potassium iodate and starch turn blue in the presence of sulphur dioxide, see "Iodic acid"

Sulphuryl chloride—If a mixture of sulphur dioxide and chlorine be exposed to direct sunlight—especially if a little camphor be present—a colourless liquid will be obtained which boils at 69° The camphor acts as a catalytic agent (p 132) The liquid is sulphuryl chloride—SO_2Cl_2 When treated with water, H—OH, the chlorine atoms in sulphuryl chloride can be replaced step by step by OH groups

$$\begin{matrix} {}^{O}_{O}\!\!\gg S & \rightarrow & {}^{O}_{O}\!\!\gg S <^{Cl}_{Cl} & \rightarrow & {}^{O}_{O}\!\!\gg S <^{OH}_{Cl} & \rightarrow & {}^{O}_{O}\!\!\gg S <^{OH}_{OH} \\ \text{Sulphur dioxide} & & \text{Sulphuryl chloride} & & \text{Chlorosulphonic acid} & & \text{Sulphuric acid} \end{matrix}$$

Chlorosulphonic acid, $SO_2Cl(OH)$—This acid is best made by the direct union of sulphur trioxide and hydrogen chloride, or by distilling a mixture of concentrated sulphuric acid with phosphorus pentachloride, PCl_5, or phosphorus oxychloride, $POCl_3$, when $2H_2SO_4 + POCl_3 = HPO_3 + HCl + 2SO_2Cl(OH)$. The liquid so obtained boils at 155 3°, and reacts with water with explosive violence, forming a mixture of sulphuric and hydrochloric acids.

Uses—Sulphur dioxide is used in the manufacture of sulphuric acid, as a refrigerating agent, as a solvent for extracting glue, gelatine, etc, for preserving meats, wines, etc It prevents the growth of certain moulds, kills certain disease germs, etc It is used for precipitating lime in sugar

manufacture, as a bleaching agent for straw, silk, woollen, and goods too delicate for treatment with chlorine, in refrigerating machines (see p 536), etc.

§ 3 The Constitution of Sulphurous Acid and the Sulphites.

> More value is sometimes attached to a formula than that which it is intended to represent In consequence of this, it has happened that a large number of chemists have regarded the determination of a formula for a compound as the great object to be accomplished, and they have forgotten that what we ought to know, and what is of vastly greater importance for the science, is the chemical conduct of the compound —I REMSEN

The empirical formula of a compound is based upon its percentage composition, and the atomic hypothesis, while a molecular formula, in addition, is coupled with Avogadro's hypothesis After the empirical and molecular formulæ have been determined, the chemical properties of the compound are studied in order to trace the relations between the atoms of the molecules, and when this has been done for all the atoms in the molecule of the substance, the **constitution of the compound** is said to have been determined The result of the investigation is expressed as a structural or graphic formula "It is assumed," as W Lossen expressed it in 1880, "that the action of any particular atom on the other atoms in the molecule depends on the relative position of the atom in question, the properties and chemical behaviour of the molecule depend upon the actions of *all* the atoms on one another Hence observations of the properties and the behaviour of a compound enable us to draw conclusions concerning the mutual actions of the atoms in the molecule of that substance, and the positions of the molecules relative to one another" A structural formula should summarize what is known about the chemical behaviour of the compound with respect to (1) the number and kind of atoms in the molecule, and (2) the relations between the atoms in the molecule

There are several possible methods of representing the constitution of sulphurous acid, and accordingly of the sulphites The sulphur may be bi-, quadri-, or sexivalent

$$\underset{\text{Sulphur dyad}}{S{<}^{O-OH}_{OH}} \qquad \underbrace{O{=}S{<}^{OH}_{OH} \qquad O{=}S{<}^{O-OH}_{H} \qquad {}^{O}_{O}{>}S{<}^{OH}_{H}}_{\text{Sulphur tetrad}} \qquad \underset{\text{Sulphur hexad}}{{}^{O}_{O}{\gg}S{<}^{OH}_{H}}$$

In one group of these formulæ, the hydrogen atoms are symmetrically placed with respect to the sulphur atom, and in the other group, the hydrogen atoms are unsymmetrical Our problem is to select from these graphic formulæ the one which best represents the orientation of the atoms in the molecule of sulphurous acid

Thionyl chloride—If dry sulphur dioxide be treated with phosphorus pentachloride, PCl_5, a colourless liquid—thionyl chloride, $SOCl_2$—boiling at 78°, is obtained[1] The initial and end products of the reaction are represented

$$O{=}S{=}O + \begin{matrix}Cl\diagdown\\ Cl{-}\\ Cl\diagup\end{matrix}P{<}^{Cl}_{Cl} = O{=}S{<}^{Cl}_{Cl} + \begin{matrix}Cl\diagdown\\ Cl{-}\\ Cl\diagup\end{matrix}P{=}O$$

[1] Thionyl chloride is also made by the action of chlorine monoxide upon sulphur at a low temperature, −12°, to prevent explosion *It is also made by* adding sulphur trioxide to sulphur monochloride.

Thionyl chloride has the empirical formula $SOCl_2$. Owing to its mode of formation from sulphur dioxide (sulphur quadrivalent), it is inferred that there is no change in valency of the sulphur atom when one of the oxygen atoms in sulphur dioxide is replaced by two chlorine atoms, and that the oxygen and two chlorine atoms are each directly attached to the sulphur. Thionyl chloride is decomposed by water, forming sulphurous acid

$$O{=}S{<}^{Cl}_{Cl} + {}^{H—OH}_{H—OH} = 2HCl + O{=}S{<}^{OH}_{OH}$$

This reaction is interpreted to mean that sulphurous acid has a similar constitution to thionyl chloride, but the two chlorine atoms of the last-named compound have been replaced by two hydroxyl groups derived from the water. Hence it is inferred that the two hydroxyl groups of sulphurous acid are directly united with the sulphur atom. Otherwise expressed

$O{=}S{=}O$	$O{=}S{<}^{Cl}_{Cl}$	$O{=}S{<}^{OH}_{OH}$
Sulphur dioxide	Thionyl chloride	Sulphurous acid

The constancy of structural arrangement.—It is commonly assumed that when an atom or group of atoms in a compound is replaced by another atom or group of atoms, the latter occupies the position vacated by the former without any essential structural change in the arrangement of the other atoms. This rule does not mean that the *relations subsisting between the atoms of the molecule are not altered* during the replacement of one atomic group by another, for the hydrogen atoms in, say, C_2H_3OCl may be more or less easily affected by certain reagents than the H atoms in, say, C_2H_3OBr. The rule of the constancy of structural arrangement, and the action of water on thionyl chloride, make it probable that the two chlorine atoms of thionyl chloride are directly replaced by two hydroxyl groups, but let us inquire

Does the molecule of sulphurous acid contain two hydroxyl groups symmetrically placed about the sulphur atom? If sulphurous acid contains its two hydroxyl groups symmetrically placed, we naturally prefer the formula HO—SO—OH. By neutralizing potassium hydrogen sulphite with sodium hydroxide, and by neutralizing sodium hydrogen sulphite with potassium hydroxide, two solutions are obtained from each of which crystalline potassium sodium sulphite can be separated. In both cases compounds with identical properties, namely, potassium methyl sulphonate, CH_3KSO_3, are obtained when the double sulphites are treated with methyl iodide, CH_3I. The reaction in each case is represented

$$CH_3I + NaKSO_3 = NaI + CH_3KSO_3$$

The methyl radicle CH_3 thus displaces the sodium atom, but not the potassium atom. Consequently, if two isomeric salts, say,

$$\underset{O}{\overset{O}{}}{\geqslant}S{<}^{OK}_{Na} \qquad \underset{O}{\overset{O}{}}{\geqslant}S{<}^{ONa}_{K}$$

are capable of existing, the one in which the atom of potassium is directly connected with the sulphur atom *is not stable and readily changes into*

the other Otherwise expressed, there is at present no evidence of the existence of two different salts $KO.SO_2.Na$ and $NaO.SO_2.K$. So far as we can tell, *the graphic formulæ of the sulphites correspond with two symmetrically placed hydroxyl groups in sulphurous acid*, and the formula is accordingly written HO—SO—OH

The "rule of the constancy of structural arrangement" might here easily lead us astray because the fact that no isomerism has hitherto been detected in the compounds prepared by the two different methods, may be due to the fact that with certain radicles only one configuration is stable and permanent If another configuration be momentarily produced it immediately passes into the stable condition Hence the negative results just obtained do not prove conclusively that an unsymmetrical sulphurous acid is non-existent, although the negative results may prove that there is only one stable configuration of $NaKSO_3$ or of CH_3KSO_3 under the conditions of the experiment

Desmotropism or tautomerism—Some compounds are known in organic chemistry which correspond with the existence of unsymmetrically placed hydroxyl groups in the sulphurous acid molecule For instance, the action of ethyl alcohol on thionyl chloride, $SOCl_2$, furnishes a compound $SO_3(C_2H_5)_2$ Since the structural formula of thionyl chloride is $O{=}S{<}^{Cl}_{Cl}$ the compound formed from it probably has the corresponding symmetrical structure $O{=}S{<}^{OC_2H_5}_{OC_2H_5}$ It is accordingly called **symmetrical diethyl sulphite**. This salt boils between 158° and 158.5° Again, the oxidation of ethyl mercaptan, C_2H_5—S—H (in which the ethyl monad radicle, C_2H_5, must be directly attached to the sulphur) furnishes a compound of the same ultimate composition, but with an unsymmetrical structure, hence, it is called **unsymmetrical diethyl sulphite** $^{O}_{O}{\gg}S{<}^{C_2H_5}_{OC_2H_5}$ This salt boils between 214° and 215° The existence of these two sulphites does not necessarily mean that there are two different sulphurous acids, for there may be but one stable configuration of the acid itself under the conditions of the experiment

It is not unlikely that under certain conditions, and by the action of certain reagents, the position of an hydrogen atom in the molecule can change so that it behaves differently under one set of conditions from what it does under another set of conditions The phenomenon appears an exception to the rule of the constancy of structural arrangement As usual, the supposed phenomenon has been given *a name*, "tautomerism" (C Laar, 1885)—from the Greek ταὐτό (tauto), the same, μέρος (meros), a part—and also the alternative, perhaps better, name, "desmotropism" (P Jacobsen, 1887)—from the Greek δεσμός (desmos), a bond, τρέπειν (trepein) to change A substance is said to be tautomeric or desmotropic when it can react with other substances in such a way that it appears to be a compound with different constitutional formulæ In any given system, the two desmotropic modifications of a substance are in a state of equilibrium which is so very sensitive to external influences that the one modification readily changes into the other A desmotropic change is thus an intra molecular phenomenon which only lends itself to observation

under exceptional conditions It is supposed that the position of a hydrogen atom in the molecule of sulphurous acid is labile, not rigid, because it can take up two different positions with respect to the other atoms The change in the position of the hydrogen atom is accompanied by a change in the character of the linkages In the present case, we have possibly

$$\begin{matrix}O\\O\end{matrix}\!\!\gg S<\begin{matrix}H\\OH\end{matrix} \rightleftharpoons O{=}S<\begin{matrix}OH\\OH\end{matrix}$$

We shall meet other examples later on—nitrous acid $H—NO_2$ and $HO—NO$, hydrocyanic acid $H—C \; N$ and $H—N \; C$, phosphorous acid $P(OH)_3$ and $H \, PO(OH)_2$, etc The supposed desmotropism of the poly sulphides has been already mentioned, p 416

§ 4 Hyposulphurous Acid and Hyposulphites

Preparation—By treating an aqueous solution of sulphur dioxide with finely divided zinc, a zinc salt of hyposulphurous acid is obtained $2H_2SO_3 + Zn = ZnS_2O_4 + 2H_2O$ By using sodium hydrogen sulphite, the sodium salt is obtained A yellow aqueous solution of the acid can be obtained by treating aqueous solutions of its salts with oxalic acid. It is probable that the zinc reacts with the sulphurous acid producing hydrogen $Zn + H_2SO_3 = ZnSO_3 + H_2$, and that the nascent hydrogen reduces the sulphurous acid to the acid in question $2H_2SO_3 + 2H = H_2S_2O_4 + 2H_2O$ The acid then reacts with the zinc producing the zinc salt The sodium salt has also been obtained in concentrated solution by the electrolysis of sodium hydrogen sulphite with a high density current By adding sodium chloride to the solution, sodium hyposulphite, $Na_2S_2O_4 \; 2H_2O$, is precipitated. This salt can be dehydrated at 60°

Properties—The acid is only known in aqueous solutions since it is rather unstable It rapidly absorbs oxygen from the air, and is one of the most powerful reducing agents known The sodium salt is used industrially, and in the chemical laboratory as a reducing agent For instance, it bleaches sugar, indigo blue, etc It reduces many metallic salts to the metal, in the case of copper sulphate, a brown copper hydride, Cu_2H_2, is formed. The salts are called **hyposulphites**[1]

Composition—The molecular weight of the acid has not been determined by the regular methods, but the molecular weight of the sodium salt, deduced from the depression of the freezing point of aqueous solutions corresponds with the formula $Na_2S_2O_4$ Again, ammoniacal copper sulphate oxidizes a hyposulphite to a sulphite, iodine oxidizes it to a sulphate, and for every two atoms of sulphur present as hyposulphite, one atom of oxygen is required to oxidize it to sulphite $S_2O_3 + O = 2SO_2$, and three atoms of oxygen to oxidize two atoms of sulphur to sulphate $2S_2O_3 + 3O_2 = 4SO_3$ Hence it is inferred that hyposulphurous acid is derived from the anhydride S_2O_3—sulphur sesquioxide—and not to the anhydride, SO, as supposed by P Schützenberger, the discoverer of the acid (1869)[2]

[1] Do not confuse the acid with thiosulphuric acid, nor the salts with thiosulphates Unfortunately, hyposulphurous acid is an old term for thiosulphuric acid which has been abandoned by all but photographers

[2] C L. Berthollet (1789) noticed that iron dissolves in sulphurous acid without giving off a gas, L N Vauquelin and A F Fourcroy (1798) found that tin and zinc behaved in a similar way, and C F Schönbein (1852) obtained some reactions with a lower sulphur acid, and which were probably due to this acid

Schutzenberger thought the acid had the formula H_2SO_2, but A Bernthsen's (1881) experiments, just cited, make it almost certain that the formula is $H_2S_2O_4$

Sulphur sesquioxide, S_2O_3, is supposed to be made as a malachite green crystalline mass by the direct union of sulphur and sulphur trioxide, and as a blue solution by the action of flowers of sulphur on Nordhausen sulphuric acid With water, sulphur sesquioxide gives sulphur and a mixture of sulphuric and sulphurous acids, and not hyposulphurous acid This does not prove that sulphur sesquioxide is not the anhydride of hyposulphurous acid because the *latter decomposes in a similar way.*

§ 5. Sulphur Trioxide—Preparation.

Sulphur trioxide exists in at least two forms, α sulphur trioxide and β-sulphur trioxide Molecular weight, α $SO_3 = 80$ 07, β $SO_3 = 160$ 14 Melting point α SO_3, 14 8°, β SO_3, 25°, boiling point of both varieties, 46 2°

History —Sulphur trioxide seems to have been made by B Valentine in the fifteenth century, and called "philosophical salt" K W Scheele (1777) and G de Morveau (1786) called it the anhydride of sulphuric acid

Preparation —Sulphur trioxide is made by distilling ferric sulphate $Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$, fuming sulphuric acid, or sodium pyrosulphate $Na_2S_2O_7 = Na_2SO_4 + SO_3$, and also by heating concentrated sulphuric acid with phosphorus pentoxide when $H_2SO_4 + P_2O_5 = SO_3 + 2HPO_3$ In the latter reaction the phosphorus pentoxide is able to dehydrate, that is, remove the elements of water from sulphuric acid

As indicated on p 418, a small amount of sulphur trioxide is formed when sulphur burns in air, or in oxygen, but if a mixture of sulphur dioxide and oxygen be passed over platinized asbestos at about 400°, the oxidation of the sulphur dioxide is nearly complete The platinized asbestos acts as a catalytic agent (p 101) Instead of platinized asbestos, ferric oxide, vanadium oxide, copper oxide, chromic oxide, pumice stone, etc, have been employed, but none are so effective as platinized asbestos The action can be illustrated by an apparatus similar to that depicted in Fig 159 The sulphur dioxide and oxygen are sent, from gas-holders, through a wash-bottle, *A*, shown on the right of the diagram, containing concentrated sulphuric acid The mixed gases travel through a tower, *B*, containing pumice stone saturated with concentrated sulphuric acid The dried mixture of oxygen and sulphur dioxide then passes over platinized asbestos, *C*, warmed to about 400°, in a hard glass tube Combination occurs, and the sulphur trioxide condenses in the tube and bottle, *D*, surrounded by a jar containing a freezing mixture, and shown on the left of the diagram

§ 6 The Properties of Sulphur Trioxide

In 1876, R Weber showed that sulphur trioxide exists in two modifications—solid and liquid at ordinary temperatures

α-Sulphur trioxide—liquid sulphur trioxide.—This is a colourless liquid, boiling at about 45°, obtained by repeated distillation of the product of the preceding reactions—§ 5 The liquid fumes strongly in air It

crystallizes in long prismatic needles between 16° and 17°, and melts at 16 8° The vapour density (air = 1) varies from 2 74 to 2 70 The numbers and the lowering of the freezing point of phosphorus oxychloride correspond with a molecular weight of 80

β-Sulphur trioxide—solid sulphur trioxide —If *α* sulphur trioxide be maintained at 16° for some time, it gradually passes into solid crystals which look like asbestos, and melt at 25° The mass fumes in air, and gradually passes into the *α* form if kept at a temperature between 50° and 100° The molecular weight b[illegible]on of the freezing point of phosphorus oxychloride correspo[illegible]

The two forms are not very different chemically although the *β* sulphur trioxide reacts somewhat less vigorously than the *α* variety Both dissolve in water with a hissing sound as if a piece of red hot iron were plunged into the water, much heat is evolved, and sulphuric acid is produced

$$\alpha\, SO_3 + H_2O = H_2SO_4 + 40 \text{ Cals}$$

Hence sulphur trioxide is also called sulphuric anhydride The anhydride does not redden blue litmus if extreme precautions be taken to

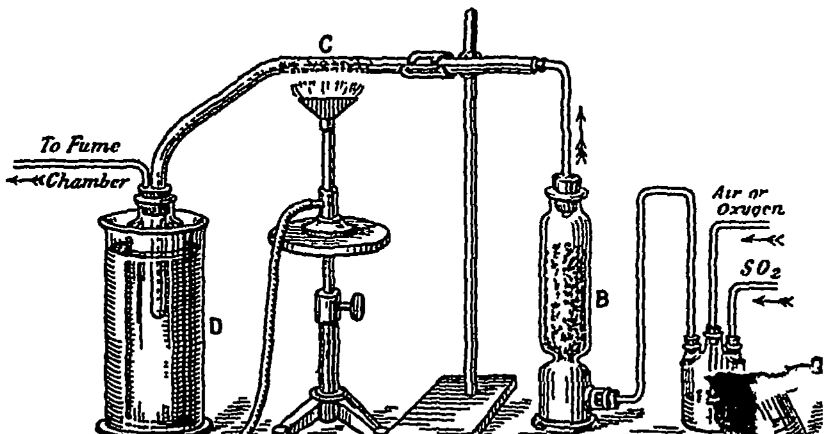
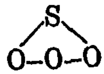


FIG 159 —Preparation of Sulphur Trioxide (Contact Process)

exclude moisture Sulphur trioxide reacts directly with many metal oxides, forming the corresponding sulphates, *e.g.* with barium oxide, $BaO + SO_3 = BaSO_4$, so much heat is evolved during the action that the mass becomes incandescent

The solid trioxide can be vaporized without melting At low temperatures, the vapour seems to contain both SO_3 and S_2O_6 molecules in equilibrium $S_2O_6 \rightleftharpoons 2SO_3$ The dissociation is completed as the temperature rises. When heated to 1000°, sulphur trioxide decomposes completely into sulphur dioxide and oxygen $2SO_3 = 2SO_2 + O_2$ Two volumes of sulphur trioxide produce two volumes of sulphur dioxide and one volume of oxygen This corresponds with the formula $(SO_3)n$ The molecular

eight of the α-form, indicated above, shows that its formula must be SO_3, and the β-form, S_2O_6. The graphic formula for SO_3 may be

$$\begin{matrix}O\\O\end{matrix}\!\!>\!S{=}O,\quad \begin{matrix}O\\|\\O\end{matrix}\!\!>\!S{=}O,\ \text{or}$$ 

which makes sulphur sexivalent, quadrivalent, or bivalent. The first formula is usually taken in harmony with the supposed sexivalency of sulphur in sulphur her[e] ... it fits in best with facts to be developed later. The graphic formulae for the two varieties will then be

$$\alpha\text{-form}\ \begin{matrix}O\\O\end{matrix}\!\!>\!S{=}O \qquad \beta\text{-form}\ \begin{matrix}O\\O\end{matrix}\!\!>\!S\!<\!\begin{matrix}O\\O\end{matrix}\!>\!S\!<\!\begin{matrix}O\\O\end{matrix}$$

The thermal values of the reactions, $S + O_2 = SO_2 + 69.26$ Cals., and of $SO_2 + O = SO_3 + 22.73$ Cals., are worthy of note. It follows that the thermal value of each of the first two oxygen atoms is 34.63 Cals., and the thermal value of the next atom of oxygen is 22.73 Cals. Hence it has been said that the third atom of oxygen is "less firmly attached" to the sulphur atom than the other two, and further that the six valencies of sulphur are not equivalent. This is supposed to correspond with the fact that sulphur trioxide is very readily dissociated into sulphur dioxide and oxygen. Some consider sulphur trioxide to be an "oxide of sulphur dioxide." The inference is inconclusive and faulty.

Occurrence.—Solutions of sulphur dioxide soon absorb oxygen from the air, forming sulphuric acid, hence sulphuric acid may be found in water from sulphurous springs in volcanic districts, *e.g.* the Rio Vinagro (Mexico) contains 0.11 per cent. of H_2SO_4 calculated as SO_3, *and also* 0.09 per cent. of HCl. Pit water and streams of water which have been in contact with oxidizing pyrites may also contain free sulphuric acid. This is often a source of trouble industrially owing to the corrosive action of such water on pump valves, etc. The occurrence of combined sulphuric acid as sulphates was indicated on p. 394.

§ 7. Pyrosulphuric Acid and Pyrosulphates

Sulphur trioxide dissolves in concentrated sulphuric acid. The solution is often called **Nordhausen or fuming** *sulphuric* **acid**. It is made by distilling dehydrated ferrous sulphate, $FeSO_4.H_2O$ (preferably with a little sulphuric acid or water in the receiver). The reaction appears to take place in two stages: $6FeSO_4.H_2O = Fe_2(SO_4)_3 + 2Fe_2O_3 + 3SO_2 + 6H_2O$, followed by $Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$. The same acid is obtained by heating sodium pyrosulphate admixed with *concentrated* sulphuric acid: $Na_2S_2O_7 + H_2SO_4 = 2NaHSO_4 + SO_3$. Sodium pyrosulphate is made by heating sodium bisulphate to about 400°: $2NaHSO_4 = H_2O + Na_2S_2O_7$. Hence the term "pyro"—from the Greek πῦρ (pyr), fire. This salt is sometimes called "*anhydrous sodium bisulphate*." The sodium bisulphate formed in the manufacture of fuming sulphuric acid is converted back to the pyrosulphate by heating it to about 400°.

Fuming sulphuric acid is a viscous, oily-looking liquid which is considered to be a solution of variable proportions of sulphur trioxide in concentrated sulphuric acid. The "*fuming*" of the acid is due to the escape of the sulphur trioxide. If the fuming acid be warmed, sulphur trioxide

is generally agreed that before the sulphuric acid is formed, the sulphur dioxide actually unites with the nitrogen oxide—say, nitrous acid—to form an "intermediate compound" It is inferred that under normal conditions the intermediate compound decomposes as fast as it is formed This inference appears to have been made because *the* elusive intermediate compound has not been isolated (p 136) At present, therefore, the known *facts* accord best with Péligot's simple hypothesis Speaking generally, whenever a question cannot be answered by an appeal to facts in the laboratory, keen, sometimes bitter, controversies are waged over schemes devised in the study In the present case, quite an array of *imaginary intermediate compounds* have been advocated—$H_2N_2SO_6$, E Divers, 1911, H_2NSO_5, F Raschig, 1911, $HNSO_5$, H. Davy, 1812, etc Taking E Diver's scheme as illustrative of current theories, the intermediate compound nitroxysulphuric acid, $H_2N_2SO_6$, is supposed to be formed by direct combination of nitrous acid with sulphur dioxide $2HNO_2 + SO_2 = H_2N_2SO_6$, and the nitroxysulphuric acid so formed is immediately decomposed into nitric oxide and sulphuric acid $H_2N_2SO_6 = 2NO + H_2SO_4$ The nitric oxide so formed is immediately oxidized to nitrogen peroxide $2NO + O_2 = N_2O_4$ This again unites with sulphur dioxide and water to reform nitroxysulphuric acid and oxygen, $2N_2O_4 + 2H_2SO_3 = 2H_2N_2SO_6 + O_2$ The nitroxysulphuric acid decomposes as indicated above and the cycle begins anew

The manufacturing process—Sulphuric acid was known to writers in the thirteenth century B Valentine, in the fifteenth century,[1] described the preparation of sulphuric acid from calcined ferrous sulphate and silica, and by burning sulphur and nitre in moist air A. Libavius (1595) recognized the identity of sulphuric acid made by the different processes, previously, the acids were supposed to be different Ward, in 1740, prepared sulphuric acid by burning sulphur with nitre in large glass vessels—40 to 60 gallons capacity—time after time, until the acid which collected on the bottom of the vessels was strong enough to pay for its concentration in glass retorts The acid was sold as "oil of vitriol made by the bell," to distinguish it from the acid made from ferrous sulphate Ward's process reduced the price of sulphuric acid from 2*s* 6*d* per ounce to 2*s* per pound. Roebuck substituted lead chambers for Ward's glass vessels in a works at Birmingham in 1746 F Clément and J B Désormes, in 1793, showed that the process could be made continuous, and that the nitre plays an intermediary part between the sulphur dioxide and the air J L. Gay Lussac's tower was invented in 1827, and J Glover's tower was used at Newcastle on Tyne in 1859

1 **The burners**—The sulphur dioxide is made in the burners, (1) by burning sulphur (brimstone), (2) by heating pyrites, etc, in a current of air, or (3) by burning hydrogen sulphide, etc Air is drawn through the burners in excess of that required for oxidizing the sulphur The necessary draught is regulated by chimney, etc

2 **The Glover's tower**—The hot mixture of air and sulphur dioxide passes up a tower packed with flints down which trickles a mixture of a weak acid from the lead chambers and the strong nitrated acid which has been used to absorb nitrous fumes, and recovered in the Gay Lussac's

[1] As in the case of Geber some writings attributed to Valentine are supposed to be forgeries

tower to be described later. The functions of the Glover's tower are: (1) recover the nitrous oxides from Gay Lussac's tower; (2) cool the gases from the burners; (3) help to concentrate the acid trickling down the tower (4) partly oxidize the sulphur dioxide from the burners, and (5) introduce the necessary nitric acid into the lead chambers by running nitric acid down the tower along with the nitrated acid from the Gay Lussac's tower[1] Before the acid reaches the foot of the tower it is fully denitrated.

3 The lead chambers—The mixture of air, sulphur dioxide and nitrous fumes passes into a set of three leaden chambers—may be of a total capacity of 150,000 cubic feet—into which steam is blown from low pressure boilers The gases in the chambers are thus intimately mixed. The oxidation of the sulphur dioxide mainly occurs in the first two chambers. The gases are passed through the chambers slowly so as to allow time for all the sulphur dioxide to be oxidized. The third chamber serves mainly to dry the gases. The chambers are kept cool enough to condense the sulphuric acid which collects on the floor and is drawn off periodically. It is called *chamber acid* Chamber acid contains between 62 and 70 per cent. H_2SO_4

4. The Gay Lussac's tower.—The excess air which leaves the lead chambers is highly charged with nitrogen oxides. These are recovered by causing the exit gases from the chambers to pass up a tower, packed with coke, down which concentrated sulphuric acid is trickling The concentrated acid absorbs the nitrous fumes. The "nitrated acid" which collects at the foot of the Gay Lussac's tower is pumped to the top of the Glover's tower along with some of the more dilute chamber acid. The "nitrated acid" trickling down the Glover's tower loses the absorbed nitrous fumes and some water The acid which collects at the foot of the tower contains about 80 per cent H_2SO_4

5 The concentration of the acid.—The chamber acid is not allowed to attain a higher strength than about 62 to 70 per cent H_2SO_4, because a stronger acid begins to absorb the nitrous fumes from the chambers. The chamber acid is therefore concentrated further either in the Glover's tower as indicated above, or in leaden concentrating pans until it contains about 79 per cent of H_2SO_4 If the acid be much stronger than this, it begins to attack the lead evaporating pans rather seriously. This acid is now called "B O V." ("brown oil of vitriol"), its usual brown colour is due to the presence of organic matter. The further concentration of the acid is effected either by boiling it in glass, vitrified quartz, or in platinum stills The acid may also be placed in these stills direct from the chambers. At first very weak sulphuric acid distils over The concentration of the acid in the still gradually rises until it has about 98 3 per cent H_2SO_4 Any further concentration cannot be done by evaporation since the acid itself then distils over. The further concentration of the acid, in the rare event of its being required, is effected by cooling the concentrated acid when crystals of 100 per cent. H_2SO_4, melting at 10 5°, separate; the acid can of course be further "concentrated" by dissolving sulphur trioxide in it—see "Fuming sulphuric acid."

[1] The gases from the Glover's tower sometimes meet a pipe bringing in nitrous fumes made by heating concentrated sulphuric acid with Chili saltpetre by the waste heat from the burners

§ 9 The Manufacture of Sulphuric Acid—Contact Process

The manufacture of sulphuric acid by the contact process can be illustrated by the apparatus depicted in Fig 159 if the jar, etc, *D*, on the left, be replaced by a tower, packed with coke, Fig 161, down which water or dilute sulphuric acid is allowed to trickle The liquid absorbs the sulphur trioxide The oxidation of the sulphur dioxide really involves two opposing reactions represented by the equation $2SO_2 + O_2 \rightleftharpoons 2SO_3$ By passing the mixed gases—air and sulphur dioxide—through a porcelain tube in the absence of platinized asbestos, about 10 per cent of sulphur trioxide is formed at 400° under the conditions of manufacture, whereas in the presence of platinized asbestos, very nearly 100 per cent is oxidized Without the platinized asbestos, a maximum 30 per cent oxidation is obtained just over 600° If the temperature, with platinized asbestos, is above or below 400°, the yield of sulphur trioxide is reduced, for instance, at 250° there is a 45 per cent. conversion, and at 1000° no sulphur dioxide is oxidized at all. The curves, Fig 162, show the effect of temperature on the yield of sulphur trioxide The presence or absence of the catalytic agent does not affect the final state of true equilibrium, but it does affect the speed at which the equilibrium is attained In consequence, the final state of equilibrium appears different with and without the platinized asbestos because the process requires an indefinite time to attain a state of equilibrium without the catalytic agent The curves, Fig 162, thus represent the per cent of sulphur trioxide formed when the mixed gases are passed slowly through a tube with and without platinized asbestos at the temperatures stated Not only is the speed of oxidation of the sulphur dioxide determined by the temperature, but it is accelerated by increasing the proportion of oxygen beyond that represented by the above equation two volumes of sulphur dioxide per one volume of oxygen Experience shows that the most efficient mixture contains three molecules of oxygen per two molecules of sulphur dioxide

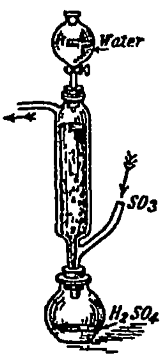


FIG 161 —Condenser for SO_3

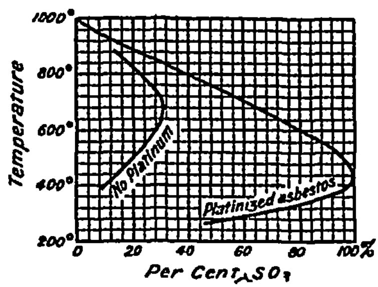


FIG 162 —Effect of Temperature on the Oxidation of Sulphur Dioxide

The manufacturing process—The contact process was the subject of a British patent by P Phillips in 1831, but it was not until seventy years later, when R Knietsch (1901) demonstrated the conditions necessary for successful work, that the contact process attained commercial success The results are now so satisfactory that the "chamber process" is considered by many to be a "threatened industry" which will have to retire in favour of the more efficient "contact process" Threatened industries

sometimes live long, because competition acts as a healthy stimulus which leads to such improvements that the threatened industry has no difficulty in maintaining its position

1 The purification of the burner gases —The mixture of sulphur dioxide and air from the "burners" must be very carefully cleaned from dust, finely divided sulphur, sulphuric acid, arsenic, etc, otherwise the platinized asbestos soon becomes inactive Arsenic is particularly injurious A very small trace of arsenic in the gases soon paralyzes—"poisons"—the activity of the platinum The gases are accordingly cleaned by passage through a chamber—the "dust chamber"—in which steam is injected, through a series of lead pipes to reduce the temperature down to about 100°, through a series of towers in each of which the gases meet a descending spray of water This washes the sulphuric acid, etc, from the gas Finally, the gases are dried by passing them up a tower where they meet a descending stream of concentrated sulphuric acid The gases are periodically tested for dust, arsenic, etc, to make sure the scrubbers, etc, are working efficiently

2 The contact chamber —The dried gases then pass into the contact chamber This is illustrated diagrammatically in Fig 163 In outline it consists of a cylinder which contains a number of tubes each packed with platinized asbestos placed between perforated shelves The dry mixture of sulphur dioxide and air enters the contact chamber through a series of perforations near the base, and, after passing up to the top of the cylinder around the outside of the tubes containing the platinized asbestos, the gases descend through the platinized asbestos (where oxidation takes place), and leave the apparatus

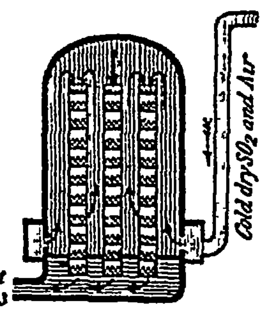


Fig 163 —Contact Chamber (Diagrammatic)

The platinized asbestos is arranged in this particular manner to avoid local rise of temperature by the heat evolved during the reaction.

$$2SO_2 + O_2 = 2SO_3 + 45\ 2 \text{ Cals}$$

Hence the system has a tendency to get hotter during the oxidation. Since the best results are obtained when the temperature of the asbestos is in the vicinity of 400°, everything is arranged so that the asbestos tubes are maintained at this temperature by the cold gases ascending in the interior of the cylinder [1] Experience shows that 96 to 98 per cent of the sulphur dioxide is oxidized in the cylinder [2]

3 The condensation of the sulphur trioxide —The "white mist" of sulphur trioxide is absorbed with great difficulty by water or dilute sulphuric acid, but it is rapidly and completely absorbed by 97 to 98 per cent sulphuric acid. Hence the gases which leave the contact chamber pass into cast-iron tanks containing 97 to 98 per cent sulphuric acid A stream of water or dilute acid is run into the condensing tanks at such a rate that the strength of the acid is maintained at 97 to 98 per cent If

[1] At the start, the asbestos is raised to the necessary temperature by heating the contact chamber from below

[2] With ferric oxide as contact agent, 60 to 66 per cent oxidation is obtained

fuming acid be required, one or more wrought iron[1] absorbing vessels are placed between the condensing tanks and the contact chamber

§ 10 The Properties of Sulphuric Acid

Contraction on dilution—When sulphuric acid is mixed in water, the volume of the cold mixture is much less than the sum of the volumes of water and acid used It is remarkable that the greatest contraction occurs with a solution containing about 97 7 per cent of H_2SO_4, that is, 79 7 per cent of SO_3 There is another maximum contraction with solutions containing 60 per cent of free sulphur trioxide, that is a total per cent of 92 65 SO_3 A curve showing the volume of one gram of different solutions of sulphur trioxide and of sulphuric acid, H_2SO_4, in water is shown in Fig 164

Boiling point—Sulphuric acid (H_2SO_4) boils at about 270° with partial decomposition Some sulphur trioxide passes off as vapour, the acid in the retort becomes weaker, and the boiling point steadily rises until the acid has attained a strength of about 98 per cent H_2SO_4 (that is, 80 per cent SO_3), when it distils over unchanged Conversely, on boiling dilute solutions of sulphuric acid, the acid becomes stronger and

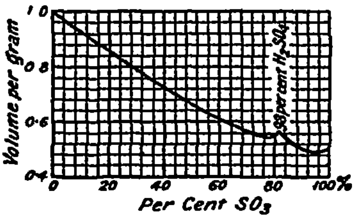


FIG 164 —Contraction Curve

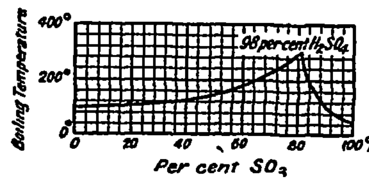


FIG 165 —Boiling Curve.

stronger since water or very dilute acid passes over, at the same time, the boiling point steadily rises as illustrated in Fig 165, until the acid has attained a strength of 98 per cent H_2SO_4, when it distils over unchanged, at 317° The monohydrate fumes slightly, owing to the evolution of a little sulphur trioxide, when heated to above 30° The facts just indicated are represented by the curve, Fig 165, where the boiling point curve shows a sharp apex at 317° Below that temperature, water or dilute sulphuric acid, and above that temperature sulphur trioxide, is evolved At that temperature (750 mm pressure) a constant boiling acid is obtained The specific gravity curve also shows a maximum, or the contraction curve a minimum (Fig 164), with an acid of nearly that concentration This acid also absorbs sulphur trioxide more rapidly—"greedily"—than either water or dilute sulphuric acid

Vapour density—The vapour of sulphuric acid is completely dissociated into water and sulphur trioxide at 450° Granting this fact, and Avogadro's hypothesis, we have

$$\underbrace{H_2SO_4}_{2\text{ vols}} = \underbrace{SO_3 + H_2O}_{4\text{ vols}}$$

[1] Experience shows that wrought iron is most efficient for the fuming acid, cast iron for the more dilute acid

The vapour density should be about half that required for H_2SO_4. The theoretical value (O = 32) for H_2SO_4 is 98, H. St. C. Deville and L. Troost (1860) found 50·03, which corresponds, very nearly, with a complete dissociation. At still higher temperatures, the sulphur trioxide itself dissociates, as indicated in the curve, Fig. 162. H. St. C. Deville and H. Debray (1860) suggested a process for the manufacture of oxygen on this reaction. They proposed to conduct the vapour of sulphuric acid through a porcelain tube filled with bits of porcelain heated to bright redness. But nothing has come of the suggestion.

Freezing-point curves.—The freezing point curves of solutions of sulphur trioxide in water are shown in Fig. 166. Maxima occur at points corresponding with $H_2SO_4.4H_2O$, $H_2SO_4.H_2O$, H_2SO_4, and $H_2SO_4.SO_3$ (pyrosulphuric acid). Our previous study of freezing point curves (pp. 161 and 230) shows that these may be taken to represent the composition of definite compounds of sulphur trioxide and water formed under the conditions stated.

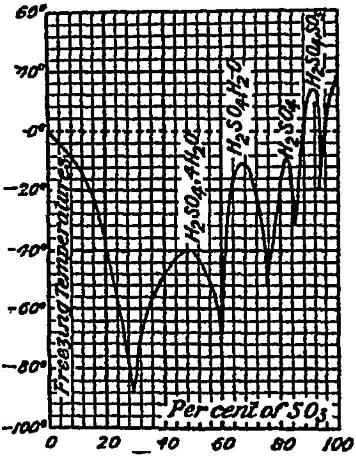


FIG. 166.—Freezing point Curve.

Hydrates of sulphur trioxide.—Several hydrates have been isolated. Pyrosulphuric acid—$H_2O.2SO_3$, or $H_2SO_4.SO_3$—forms a transparent crystalline mass melting at 35° (p. 430). Monohydrated sulphuric acid[1]—$SO_3.H_2O$, or H_2SO_4—is a limpid colourless liquid without smell, with a specific gravity 1·850 at 15°, and 1·822 at 45°. It solidifies at 0°, forming crystalline plates which melt at 10°. Dihydrated sulphuric acid—$SO_3.2H_2O$, or $H_2SO_4.H_2O$—crystallizes in hexagonal prisms, melting at 8°. Pentahydrated sulphuric acid—$SO_3.5H_2O$, or $H_2SO_4.4H_2O$—melts at −25°. Trihydrated sulphuric acid—$SO_3.3H_2O$, or $H_2SO_4.2H_2O$—corresponds with a minimum point on the curve, and must therefore be regarded as a eutectic mixture under the conditions of the experiment (*cf.* p. 231). This does not mean that a hydrate $H_2SO_4.2H_2O$ will not exist under other conditions. Several claim to have isolated $H_2SO_4.2H_2O$ as a white crystalline mass, melting at about −70°.

The heat of dilution.—When sulphuric acid and water are mixed a considerable rise of temperature occurs. The curve for the heat of solution rises steadily from 3·9 Cals. with 61·25 per cent. H_2SO_4, to 19·3 Cals. with 100 per cent. H_2SO_4, and to 19·9 Cals. with sulphuric acid containing 2 per cent. of sulphur trioxide in solution, to 48·6 Cals. with 100 per cent. free sulphur trioxide. Hence sulphuric acid and water should be mixed with care. Do not pour the water into the acid, but always pour the acid into the water with constant stirring.

Absorption of water by sulphuric acid.—The great affinity of sulphuric acid for water is evidenced by its hygroscopicity and its use in desiccators, and in the balance case for keeping a dry atmosphere in these vessels; and also for drying gases. Sulphuric acid acts upon many solid

[1] Many writers, probably more correctly, call $H_2SO_4.H_2O$ the "monohydrate," etc.

and liquid substances depriving them of water, or even decomposing the substance—splitting off the elements of water when no ready formed water is present Wood, paper, sugar, starch, and many organic substances are blackened by concentrated sulphuric acid owing to the separation of carbon which accompanies the removal of the elements of water This property is utilized (p 681) for the preparation of carbon monoxide, (p 695) for the preparation of ethylene The effect is easily demonstrated by stirring 10 grams of powdered cane sugar with 12 grams of concentrated sulphuric acid in a beaker The sugar first becomes pale brown, rapidly darkens in tint, and finally becomes black, at the same time, much steam is evolved and the mass swells up considerably

Action on metals—Sulphuric acid is an oxidizing agent, particularly in hot concentrated solutions Witness the preparation of sulphur dioxide by the action of hot concentrated sulphuric acid on copper, carbon, sulphur, etc The cold concentrated acid does not perceptibly attack copper, mercury, antimony, tin, lead, and silver, but these metals are attacked by the hot concentrated acid The prolonged action of sulphuric acid on mercury is said to give mercurous sulphide, mercuric sulphate, and sulphur dioxide, gold, platinum, iridium, and rhodium are not appreciably affected by the acid hot or cold Dilute sulphuric acid dissolves magnesium, zinc iron, cobalt, cadmium, manganese in *the cold*, forming a sulphate of the metal and hydrogen The concentrated acid has very little action on these metals in the cold, a few bubbles of hydrogen may be evolved, but the action soon appears to stop When heated, these metals give sulphur dioxide and the corresponding sulphates Warm, not cold, concentrated sulphuric acid is reduced by hydrogen, particularly in the presence of sulphates and the platinum metals Impure hydrogen, even in the cold, reduces the acid, forming a trace of sulphur dioxide It is necessary to bear this in mind when drying hydrogen with concentrated sulphuric acid

Solubility of lead sulphate—100 grams of sulphuric acid containing 95 6 per cent of sulphuric acid dissolve 0 039 gram of lead sulphate, 100 grams of 86 0 per cent sulphuric acid dissolve 0 011 gram, and 100 grams of 63 4 per cent. sulphuric acid dissolve 0 003 gram of lead sulphate The amount of lead sulphate dissolved by more dilute solutions, say 2 per cent sulphuric acid, can scarcely be detected The diminishing solubility with increasing dilution is illustrated by the separation of lead sulphate as a white cloud when sulphuric acid, which has been in contact with lead vessels, is diluted with water

§ 11 The Constitution of Sulphuric Acid and the Sulphates

> I am convinced that all theories on the constitution of organic compounds, and all controversies as to this or that mode of writing formulæ, if not supported by a plausible arrangement of the compound atom, will aid us but little in the acquisition of correct ideas —L GMELIN (1848)

It will be obvious from our study of the constitution of sulphurous acid, that a chemical formula aims at representing the chemical nature of the compound in the simplest possible manner The formula is intended to describe the way the compound behaves when it reacts with other compounds, and to show, at a glance, its relations with analogous compounds Sulphuric acid, for example, is said "to contain two hydroxyl groups," meaning that in certain reactions, the OH groups can be exchanged

for equivalent radicles, that there are certain relations between this acid and all other acids containing OH groups, etc C Schorlemmer has said that the structural formula shows "the past and future of a compound," that is, "the relation subsisting between its progenitors and its progeny" The formula for sulphuric acid is expressed $SO_2(OH)_2$ for the following reasons —

First —Chlorine can react with concentrated sulphuric acid, forming chlorosulphonic acid $Cl—HSO_3$, where one OH group in sulphuric acid is replaced by chlorine Phosphorus pentachloride—PCl_5—can displace two OH groups in sulphuric acid, forming sulphuryl chloride $Cl—SO_2—Cl$ Both these chloro compounds react with water, forming sulphuric acid The two OH groups can likewise be replaced with other radicles, *e g* NH_2 Since two OH groups can be displaced together or separately, we infer from the rule of the constancy of structural arrangement that (1) sulphuric acid—H_2SO_4—contains two hydroxyl—OH—groups

Second —Like sulphurous acid, it is possible to make but one compound, $CH_3O—SO_2—OK$, by replacing the hydrogen of the hydroxyl groups with the radicles CH_3 and C_2H_5 Hence it is inferred (2) the hydroxyl groups are related to the remainder of the atoms in the molecule H_2SO_4 in a symmetrical manner

Third —Certain univalent hydrocarbon radicles—C_2H_5, C_6H_5, etc —can replace the chlorine in $ClHSO_3$ and in SO_2Cl_2 to form, say, ethyl sulphonic acid—$C_2H_5.SO_2.OH$, and diphenylsulphone—$(C_6H_5)_2SO_2$, respectively The same compounds can be made by the oxidation of mercaptan—$C_2H_5.SH$, and of diphenyl sulphide—$(C_6H_5)_2S$, in which the radicle must be joined directly to the sulphur atom Assuming that the radicles remain fixed to the sulphur atom during the oxidation, it is inferred that (3) the hydroxyl groups in sulphuric acid—H_2SO_4—are directly attached to the sulphur atom Hence the formula $HO—SO_2—OH$ is preferable to $HO—O—S—O—OH$ for sulphuric acid.

Last —We have not yet discussed whether the SO_2 group is constituted

$$\begin{matrix} O \\ O \end{matrix}\!\!\gg\! S \!<\!\begin{matrix} OH \\ OH \end{matrix} \quad \text{or} \quad \begin{matrix} O \\ O \end{matrix}\!\!> S <\!\begin{matrix} OH \\ OH \end{matrix}$$

The sexivalency of sulphur in sulphur hexafluoride—SF_6—points to the sexivalency of the sulphur atom in the sulphates, and hence it is probable that (4) each of the two oxygen atoms is attached to the sulphur atom by a double valency For these reasons, the constitutional formula of sulphuric acid is written.

$$\begin{matrix} O \\ O \end{matrix}\!\!\gg\! S \!<\!\begin{matrix} OH \\ OH \end{matrix}$$

always remembering that it is very probable that the best of our structural formulæ is not so closely related to the actual orientation of the atoms in the molecule as the stuffed and dried specimens of a museum are related to the living organisms The three hydrates of sulphur trioxide—H_2SO_4, $H_2SO_4.H_2O$, and $H_2SO_4.2H_2O$—are sometimes written graphically

$$\underset{SO_3}{\begin{matrix} O \\ O \end{matrix}\!\!\gg\! S{=}O} \qquad \underset{H_2SO_4}{\begin{matrix} O \\ O \end{matrix}\!\!\gg\! S \!<\!\begin{matrix} OH \\ OH \end{matrix}} \qquad \underset{H_2SO_4.H_2O}{\begin{matrix} HO \\ HO \\ O \end{matrix}\!\!\gg\! S \!<\!\begin{matrix} OH \\ OH \end{matrix}} \qquad \underset{H_2SO_4.2H_2O}{\begin{matrix} HO \\ HO \\ HO \end{matrix}\!\!> S <\!\begin{matrix} OH \\ OH \\ OH \end{matrix}}$$

There is not yet much experimental evidence in support of the two latter formulæ, and the method does not help us in dealing with the hydrate $H_2SO_4 \cdot 4H_2O$, nor in understanding how these acids are all dibasic

§ 12. Sodium, Potassium, Mercury, and Copper Sulphates

Sulphuric acid produces salts—sulphates—when it acts upon certain metals, metallic oxides, hydroxides, and carbonates The sulphates are also prepared by heating salts of the more volatile acids—chlorides, nitrates, etc —with sulphuric acid Sulphuric acid is dibasic, forming two series of salts—normal and acid sulphates, p 140

$\begin{matrix} O \\ O \end{matrix} \gg S < \begin{matrix} OH \\ OH \end{matrix}$	$\begin{matrix} O \\ O \end{matrix} \gg S < \begin{matrix} ONa \\ OH \end{matrix}$	$\begin{matrix} O \\ O \end{matrix} \gg S < \begin{matrix} ONa \\ ONa \end{matrix}$
Sulphuric acid	Sodium acid sulphate	Sodium normal sulphate

The sulphates are usually fairly soluble in water, and crystallize readily The sulphates of lead, calcium, strontium, and barium are but sparingly soluble in water

Sodium and potassium sulphates —The salts can be prepared by the general methods—action of acids on the corresponding bases, etc. While sodium sulphate crystallizes in monoclinic prisms with 10 molecules of water of crystallization the potassium sulphate forms anhydrous rhombic prisms The solubility of sodium sulphate has been discussed in connection with Fig 54 Both sodium and potassium form acid sulphates —triclinic $KHSO_4$ and rhombohedral $NaHSO_4$—when heated with sulphuric acid, and the mixture allowed to cool Acid sodium sulphate is less soluble in water than the corresponding potassium salt Thus, 100 grams of water at 25° dissolve 55 3 grams of $KHSO_4$, and 28 6 grams $NaHSO_4$, while at 100° the numbers are 121 6 and 50 0 respectively Many minerals which resist attack by acids are broken down by fusion with the acid sulphates When, say, acid potassium sulphate is fused, water is evolved and **potassium pyrosulphate**, $K_2S_2O_7$—also written $K_2SO_4 \cdot SO_3$, or $K_2O \cdot 2SO_3$—is formed $2KHSO_4 = H_2O + K_2S_2O_7$ Some more complex acid salts are known $K_2O \cdot 4SO_3$, and $K_2O \cdot 8SO_3$ Sodium does not form higher acid salts than the pyrosulphate

Manufacture of sodium and potassium sulphates —(1) *Leblanc's salt-cake process* —Large quantities of sodium sulphate are made in Leblanc's salt-cake process by warming sodium chloride with sulphuric acid in large cast-iron pans $NaCl + H_2SO_4 = NaHSO_4 + HCl$ The torrents of hydrogen chloride which are given off are led through condensing towers for the preparation of hydrochloric acid After the first action is over, and the mixture in the pans begins to stiffen, the solid mass is raked on to the hearth of a reverberatory furnace and roasted by passing the hot gases from burning coke over the mass In this way, most of the sodium acid sulphate is converted into the normal sulphate $NaHSO_4 + NaCl = Na_2SO_4 + HCl$ The greater part of the hydrochloric acid from the sodium chloride comes from the pans—" pan gas "—and the remainder is evolved during the roasting—" roaster gas " The result of these operations is called " salt-cake " Salt-cake contains about 95 to 96 per cent of normal sodium sulphate, and 4 per cent of a mixture of sodium chloride, acid sodium sulphate, and other impurities which were associated

with the original sodium chloride Salt-cake is used in the manufacture of sodium carbonate Potassium sulphate, if desired, can be made in the similar way from potassium chloride

(2) **Hargreaves' process**—This process for the conversion of sodium chloride into sodium sulphate avoids the intermediate formation of sulphuric acid. The gases from the pyrites burners—sulphur dioxide and air—are passed through a series of cast-iron cylinders in which the sodium chloride is heated to 500° or 560° In a few days, the conversion of the chloride to sulphate is practically complete $4NaCl + 2SO_2 + O_2 + 2H_2O = 2Na_2SO_4 + 4HCl$

(3) **Sodium sulphate from kieserite**—Sodium sulphate is made by mixing solutions of magnesium sulphate (from native kieserite) with sodium chloride Double decomposition occurs $2NaCl + MgSO_4 = MgCl_2 + Na_2SO_4$ On cooling the mixture, crystals of sodium sulphate are deposited from the solution

(4) **Potassium sulphate from kainite.**—Potassium sulphate can be prepared from the crystals of $K_2SO_4.MgSO_4.6H_2O$ which remain when a hot saturated solution of kainite—$K_2SO_4.MgSO_4.MgCl_2.6H_2O$—is cooled The double sulphate of magnesium and potassium is treated with the necessary amount of potassium chloride, when crystals of normal potassium sulphate separate from the solution, the mother liquid retains the more soluble double salt—$KCl.MgCl_2$

Mercurous and Mercuric sulphates—These two salts can be made by heating mercury with sulphuric acid Here, as is generally the case in preparing mercury salts, if the metal be in excess, mercurous salt is produced—Hg_2SO_4, and if the acid be in excess, the mercuric salt—$HgSO_4$—is formed Mercuric sulphate decomposes when heated, forming mercurous sulphate Basic salts are formed when mercuric sulphate is brought in contact with water, *e g* "turpeth mineral," $2HgO.HgSO_4$, is formed as a yellow powder when mercuric sulphate is digested with boiling water

Cupric sulphate—Cuprous sulphate—Cu_2SO_4—has already been discussed, p 388 When copper oxide or metallic copper is dissolved in sulphuric acid, blue triclinic crystals of copper sulphate—$CuSO_4.5H_2O$—separate from the saturated solution on cooling The crystals are also called "blue vitriol," and they are prepared on a large scale by heating scrap copper in a furnace, sulphur is thrown on to the red hot metal to form copper sulphide—Cu_2S, air is then admitted, and the sulphide is oxidized to the sulphate Copper sulphate is also made by roasting copper sulphide ores so that most of the iron is oxidized The mass is then digested with "chamber sulphuric acid", copper oxide dissolves much more quickly than iron oxide The small amount of ferric sulphate found in the resulting solution is not objectionable for many of the applications of copper sulphate Copper and iron sulphates cannot be separated by fractional crystallization because a double sulphate is deposited from solutions containing relatively large quantities of iron sulphate To purify copper sulphate from iron, metallic copper is precipitated by dipping plates of clean iron into the solution, the resulting metal is dissolved in sulphuric acid, or calcined with sulphur as indicated above

The properties of copper sulphate.—At 100° the blue crystals of

$CuSO_4.5H_2O$ lose four molecules of water, and the residual monohydrate —$CuSO_4.H_2O$—is bluish white At 230° white anhydrous copper sulphate —$CuSO_4$—is formed. The anhydrous sulphate is very hygroscopic, and it turns blue by the absorption of moisture Hence anhydrous copper sulphate is used as a test for small amounts of water, and also for drying gases More precise ideas on the dehydration of copper sulphate will be developed in the next section Copper sulphate is used in electroplating, in electric batteries, dyeing, calico printing, preserving timber, as a germicide and insecticide for trees, and in the purification of certain types of drinking water

Basic copper sulphates—By digesting copper sulphate with copper oxide, for a long time in air, a yellow powder of $CuSO_4.CuO$ is formed This basic sulphate, when thrown into cold water, forms a green insoluble compound—$CuSO_4.3Cu(OH)_2$, and in boiling water—$CuSO_4.2Cu(OH)_2$

Ammonio-copper sulphates—When ammonia gas is passed into an aqueous solution of copper sulphate, the precipitate which first forms redissolves, and a deep blue solution is obtained when an excess of ammonia has been added This solution deposits blue rhombic crystals, which, when dried over lime, have the composition $CuSO_4(NH_3)_4.H_2O$ The crystals decompose on exposure to the air, and, when heated to 149°, pass into $CuSO_4.2NH_3$, at 203°, into $CuSO_4.NH_3$, and at 260°, into anhydrous $CuSO_4$ The salt $CuSO_4.NH_3$ is also formed when ammonia gas is brought in contact with anhydrous copper sulphate

§ 13. The Vapour Pressure of Hydrates

If a substance can form a number of definite hydrates, at any given temperature, each hydrate has its own characteristic vapour pressure For instance, copper sulphate forms three hydrates with vapour pressures, at 50°

Compound	Formula	Vapour Pressure
Water alone	H_2O	92 0 mm
Pentahydrate	$CuSO_4.5H_2O$	47 0 mm
Trihydrate	$CuSO_4.3H_2O$	30 0 mm
Monohydrate	$CuSO_4.H_2O$	4 5 mm

Suppose that water vapour be slowly admitted to a "closed" vessel containing anhydrous copper sulphate at 50°, the vapour pressure will remain *constant and fixed* at 4 5 mm until *all* the anhydrous copper sulphate has been transformed into the monohydrate $CuSO_4 + H_2O \rightleftharpoons CuSO_4.H_2O$, any further addition of water vapour will be followed by a rise in the vapour pressure which will remain constant and fixed at 30 mm until all the monohydrate has been transformed into the trihydrate $CuSO_4.H_2O + 2H_2O \rightleftharpoons CuSO_4.3H_2O$ Further additions of water vapour will be attended by a rise of the vapour pressure to 47 mm and the vapour pressure will remain stationary until all the trihydrate has been transformed into the pentahydrate $CuSO_4.3H_2O + 2H_2O \rightleftharpoons CuSO_4.5H_2O$ Any further addition of water vapour will raise the vapour pressure until

the water condenses to a liquid and gives the vapour pressure of a saturated solution of copper sulphate at 50° Further additions of water vapour will simply increase the amount of condensed water When all the copper sulphate has dissolved, the vapour pressure will be determined by the concentration of the solution of copper sulphate

Conversely, starting with the pentahydrate, the reverse change will occur if water be continually withdrawn from the system The vapour pressure of the pentahydrate, 47 mm at 50°, will be maintained as long as the system contains any of the pentahydrate When all the pentahydrate has decomposed, the vapour pressure will drop suddenly to 30 mm and remain stationary until all the trihydrate has decomposed, the vapour pressure will then fall abruptly to 4 5 mm and remain at that value until all the monohydrate has decomposed into anhydrous copper sulphate These changes are usually shown diagrammatically by curves resembling Fig 167 Amounts of water, expressed in gram-molecules, are represented on the horizontal axes, and the vapour pressures along the vertical axes The constancy of the vapour pressure of each hydrate is emphasized by the horizontal terraces on the vapour pressure curve

This step by-step dissociation of the hydrates furnishes a method which is sometimes available for deciding whether or not definite compounds exist at definite temperatures If definite compounds are produced, the gradual addition or removal of water vapour will alter the vapour pressure curve until a pressure is reached which remains constant for a certain period, and then suddenly assumes a new constant value It must be added that some (*e g* P Blackman, 1911) consider the dehydration of copper sulphate pentahydrate is comparable with the removal of water from an ordinary aqueous solution, and that the "breaks" in the curve are due to a mal-interpretation of imperfect experiments This, however, does not interfere with the principle involved By measuring the rate of decomposition of hydrated aluminium and ferric hydroxides, W Ramsay inferred the non-existence of definite hydrates, but he concluded that two were formed with lead oxide—$2PbO.H_2O$, and $3PbO.H_2O$ J M. van Bemmelen, for similar reasons, believed in the non existence of definite hydrates of silicic acid The principles just described can also be applied to compounds of ammonia with silver chloride, copper sulphate, copper chloride, etc

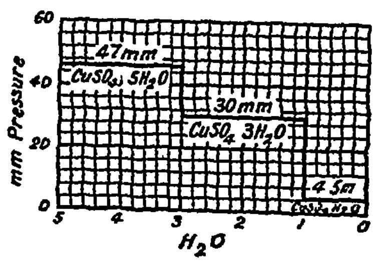


FIG 167 — Vapour Pressure Curves of the Hydrates of Copper Sulphate

§ 14 Water of Crystallization

The study of copper sulphate, which is typical of numerous other hydrates, shows that although the *molecules* of the combined water may differ in the tenacity with which they are retained by the molecule of copper sulphate, yet the water of one hydrate does not differ in kind from that of the other hydrates This water is sometimes conventionally styled "constitutional water," "water of crystallization," "water of hydration," or

"water of combination" The actual term used does not matter very much provided it is not misunderstood The mode of writing the formulæ—$CuSO_4\ 5H_2O$, $Na_2SO_4\ 10H_2O$—and the ease with which the hydrates dissociate into water, etc, might give rise to the idea that the water molecule exists in the hydrate ready-made There is however, no evidence how the elements of water are combined in the hydrate We know very little beyond the simple fact that water is a product of the dissociation of the hydrates

If the term "water of crystallization" be carelessly employed, it may suggest that crystallization is somehow dependent on the presence of water, and this the more, as efflorescent salts "appear" to lose their crystalline character when water is lost Crystals of gypsum—$CaSO_4\ 2H_2O$—form a white chalky powder when the water is driven off, crystalline sodium carbonate, and also Glauber's salts, likewise produce white powders when their combined water is expelled The powdered dehydrated substances are all crystalline In fact, practically all chemical compounds can be crystallized Crystallization is not dependent upon the presence of water Sulphur, common salt, iodine, potassium chlorate, potassium sulphate, and numerous other crystalline substances do not contain the elements of water Again crystalline calcspar does not contain the elements of water, and yet when calcined it gives a white powder The calcspar has lost carbon dioxide, not water

To prevent any misunderstanding the student should here make sure that he is perfectly clear about the use of the terms anhydrous and anhydride The latter term, in inorganic chemistry, is applied to those oxides which unite with water to form an acid, while "anhydrous" is an adjective applied to oxides salts etc, when it is desired to emphasize the fact that they do not contain the elements of water—water of crystallization, water of combination, etc

Alcohol, C_2H_5OH, has a constitution similar to water, but one of the hydrogen atoms of water is replaced by the radicle C_2H_5 Both alcohol and hydrogen peroxide can combine with certain other molecules to form complexes, and thus we speak of "alcohol of crystallization," and "hydrogen peroxide of crystallization"

§ 15 Calcium, Barium, Strontium, Magnesium, Zinc, Ferrous and Lead Sulphates

Calcium sulphate—This salt is a by product in some chemical processes It occurs in nature in white masses as *gypsum*—$CaSO_4\ 2H_2O$ It is used as a fertilizer under the name "land plaster," and also in the manufacture of plaster of Paris If the gypsum occurs in clean fine grained masses, it is called *alabaster* and if in colourless translucent crystals, *selenite*. An anhydrous form of calcium sulphate also occurs native in rhombic crystals, it is called *anhydrite*—$CaSO_4$ There is also a variety of anhydrous calcium sulphate which is made artificially, and which is more soluble than native anhydrite Artificial anhydrite is an unstable variety

In 1765 A L Lavoisier proved that gypsum is a compound of sulphuric acid and lime, and later analyses of the purest varieties show that gypsum is composed of 79 1 per cent of calcium sulphate, and 20 9 per cent of water. When these numbers are transferred into a molecular

ratio, by dividing the weight by the molecular weights of calcium sulphate and water respectively, the empirical formula for gypsum corresponds with that indicated above—$CaSO_4 \, 2H_2O$

The action of water on calcium sulphate—The solubility of calcium sulphate varies in an unusual manner with changes of temperature, for it gradually increases up to 38°, and then diminishes as illustrated in Fig 168 A hydrate in the presence of its solution is stable if it be less soluble than the other hydrates (or the anhydrous salt), in other words, if a salt forms several hydrates, that hydrate will be stable which is in equilibrium with the weakest solution For instance, below 32 8°, a solution saturated with $Na_2SO_4 \, 10H_2O$ is less concentrated than a solution saturated with the anhydrous salt, and accordingly, $Na_2SO_4 \, 10H_2O$ is the stable compound, above 32 8° the solution of anhydrous sodium sulphate is less concentrated than a solution of $Na_2SO_4 \, 10H_2O$, and therefore the anhydrous salt is the more stable form

Again, a hydrate will be stable in the presence of a solution if the vapour pressure of the hydrate be less than the vapour pressure of the solution with which it is in equilibrium If the vapour pressure be greater, the solid phase changes to the hydrate possessing the next lowest vapour pressure The hydrate with the largest proportion of water and the smallest vapour pressure will be formed in the coldest solution For instance, above 32 8°, the vapour pressure of $Na_2SO_4 \, 10H_2O$ in contact with anhydrous sodium sulphate is greater than the vapour pressure of the solution saturated with anhydrous sodium sulphate, and therefore Glauber's salt, $Na_2SO_4 \, 10H_2O$, changes into the solid anhydrous salt and its saturated solution The vapour pressure of an aqueous solution of anhydrite, $CaSO_4$, at ordinary temperatures is greater than the vapour pressure of an aqueous solution of gypsum, $CaSO_4 \, 2H_2O$ Hence, gypsum will be deposited from such a solution, and solid anhydrite placed in the solution will pass into gypsum

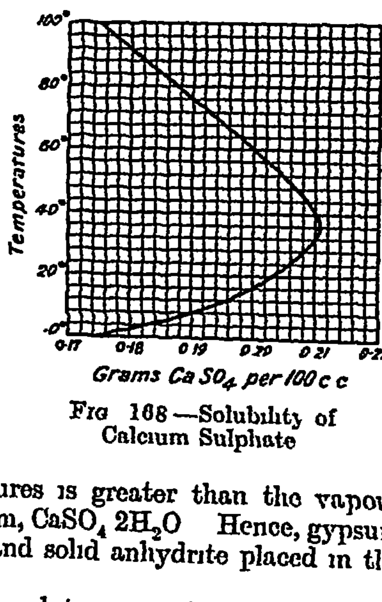


Fig 168—Solubility of Calcium Sulphate

The usual effect of a foreign salt on a solution is to lower the vapour pressure of the solution at a given temperature This may cause the formation of a lower hydrate Thus the vapour pressure of solutions of calcium sulphate containing much sodium and magnesium chlorides is lower than the vapour pressure of a solution of gypsum, and accordingly, anhydrite is deposited from such solutions, again, if gypsum be placed in the solution, it will pass into anhydrite For instance, gypsum in contact with pure water changes into anhydrite at about 66°, but in contact with a saturated solution of sodium chloride, the inversion temperature, $CaSO_4 \, 2H_2O = 2H_2O + CaSO_4$, is as low as 30°, while if other salts are present, the inversion temperature may be still lower This explains the formation of anhydrite when the Stassfurt deposits were laid by the natural evaporation of sea-water If anhydrite does occur in nature, it generally

occurs in deep seated regions protected from moist air If it occurs near the surface, and is so brought in contact with moisture, it is always associated with gypsum into which it is slowly changing The presence of anhydrite in the Stassfurt deposits was inexplicable until these facts were discovered The absence of the hemihydrate was also puzzling until it was found that the hemihydrate is in an unstable condition if other more stable forms are present, when it slowly changes into gypsum or anhydrite if one of these salts be in contact with it The hemihydrate is stable under a wide range of conditions if the more stable anhydrite or gypsum be absent

Plaster of Paris —When gypsum is heated to about 120° it loses the equivalent of $1\frac{1}{2}$ molecules of water, and forms a hemihydrate, $(CaSO_4)_2H_2O$, as a white powder called *plaster of Paris*—because of the large deposits of gypsum employed for the manufacture of plaster at Montmartre (Paris) The transformation or inversion temperature

$$2CaSO_4 \, 2H_2O \overset{107^\circ}{\rightleftharpoons} (CaSO_4)_2H_2O + 3H_2O$$

is 107° If gypsum be heated with water under pressure at 150° "silky" needle like crystals of the hemihydrate are formed. Hence this hydrate is said to occur in "boiler deposits" when water containing gypsum in solution is heated in steam boilers The hemihydrate is unstable as indicated above Plaster of Paris is a mixture of the anhydrous, dihydrate, and hemihydrate, and hence it is an unstable system The change of the hemihydrate into anhydrite and gypsum is so very slow at ordinary temperatures that the setting qualities are not lost by prolonged storage out of contact with air

When plaster of Paris is wetted with, say, one third of its weight of water, it forms a plastic mass which "sets" in from 5 to 15 minutes to a white, porous, hard mass Plaster of Paris is a valuable material for making exact reproductions of statues, ornaments, moulds, decorative work, etc. The slight expansion which occurs during the setting of plaster of Paris enables it to make a sharp reproduction of the details of a mould Different grades are used for wall plasters, cements, paper sizings, etc Admixtures of borax, alum, etc, with the plaster retard the rate of setting, while common salt, etc, accelerate the rate of setting Alum makes "set" plaster much harder—the mixture of plaster with alum is called *Keene's cement*, while a mixture with borax is called *parian cement*, and a mixture of plaster with hydraulic lime is called *Scott's selenitic cement*

Plaster of Paris, in setting, reforms a mass of interlacing needle like crystals of the dihydrate. Good plaster of Paris probably contains a mixture of the dihydrate, hemihydrate, and the anhydrous salt Anhydrous calcium sulphate is more soluble than the dihydrate, and accordingly when water is mixed with the plaster, the anhydrite dissolves first, and passes into the dihydrate This recrystallizes about the undissolved particles of the dihydrate in needle like crystals

If plaster of Paris be heated above 200°, it passes into anhydrous calcium sulphate which does not harden and set because it takes up water very slowly This is the so called "dead burnt" plaster A Potylitzin called this β $CaSO_4$ to distinguish it from the α $CaSO_4$, formed between 120° to 200°, which readily takes up water and hardens According to Rohland, another soluble form, similar to, if not the same as α $CaSO_4$,

is formed when gypsum is heated to about 520° This is the "Estrich-Gyps" or "flooring plaster" of the Germans, so named because it is largely used in Germany for making floors The slower rate of setting of the hard-fired plasters is probably due to (1) delayed recrystallization of the dihydrate owing to supersaturation, and (2) to the slower rate of solution of the anhydrite calcined at a high temperature The texture of the "set" plaster is thus dependent on the rate of setting, which is in turn dependent upon the composition of the plaster, that is, on the temperature of calcination, impurities in the native gypsum used in making the plaster, etc

Barium and strontium sulphates —Native strontium sulphate—$SrSO_4$—is called *celestine* Barium sulphate occurs in nature as *barytes* or *heavy spar* which occurs in large rhombic prisms Crystals of anhydrite and of the barium and strontium sulphates can be made by deposition from solutions in hot concentrated sulphuric acid Barium, strontium, and lead sulphates are isomorphous They form mixed crystals with one another, but calcium sulphate does not form mixed crystals with the others Barium and strontium sulphates are formed as heavy white precipitates when sulphuric acid, or a soluble sulphate, are added to solutions of barium or strontium salts respectively The precipitates are very sparingly soluble in water Comparing the solubilities of barium, strontium, and calcium sulphates 100 grams of water at 10° dissolve 0 19 gram of $CaSO_4$—calcium sulphate, 0 10 gram of $SrSO_4$—strontium sulphate, and 0 0002 gram $BaSO_4$—barium sulphate The low solubility of barium sulphate is utilized for the detection and determination of both barium and sulphuric acid. If a soluble sulphate be added to a soluble barium salt, the barium will be precipitated as barium sulphate; and conversely, if a soluble barium salt be added to a soluble sulphate, the "sulphate" will be precipitated as barium sulphate Barium sulphate is fairly soluble in hot concentrated sulphuric acid, and the solution, on cooling, deposits an acid barium sulphate—$BaSO_4 H_2SO_4$ The solution also deposits the normal sulphate as a white precipitate when diluted with water

Barium sulphate is used as a source of the barium salts—one method of transformation was discussed in connection with barium chloride, in a second process, the barium sulphate is fused with sodium carbonate $BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$ The sodium sulphate can be leached out with water, and barium carbonate remains as a residue This can be dissolved in the acid necessary for the production of the required salt If the product of the reaction be treated with an acid, before washing out the sodium sulphate, the barium salt, formed by the action of the acid on the carbonate, will at once react with the soluble sulphate and regenerate insoluble barium sulphate Barium sulphate is employed under the name "permanent white" in the manufacture of paint, as a filling for writing paper, etc

Magnesium sulphate, $MgSO_4$ —Magnesium sulphate occurs as *kieserite*, $MgSO_4 H_2O$, in the Stassfurt deposits When kieserite is digested with water, and the solution purified by recrystallization, colourless rhombic prisms of the heptahydrate—$MgSO_4 7H_2O$—separate from the cold solution When the temperature is about 30°, monoclinic prisms of the hexahydrate —$MgSO_4 6H_2O$—are formed Several hydrates are revealed when magnesium sulphate is studied by the method employed for ferric chloride.

At 150° the crystalline salt passes into the monohydrate—$MgSO_4.H_2O$, and at 200° the anhydrous salt is obtained. Magnesium sulphate forms a series of double salts—$MgSO_4.K_2SO_4.6H_2O$, *schonite*—crystallizing in monoclinic prisms, isomorphous with $MgSO_4.7H_2O$. Like barium sulphate, crystals of the acid salt $MgSO_4.H_2SO_4$ are deposited from a hot solution of magnesium sulphate in sulphuric acid, and from cold solutions, the acid salt $MgSO_4.3H_2SO_4$ is crystallized. Crystalline magnesium sulphate—$MgSO_4.7H_2O$—is also called "Epsom salts," because it occurs abundantly in the water of the Epsom springs. This salt is used in medicine, in the tanning and dyeing industries, and in the manufacture of paints and soaps.

Ferrous sulphate, $FeSO_4$.—The rhombic prisms of $MgSO_4.7H_2O$ are isomorphous with the corresponding salts of zinc—$ZnSO_4.7H_2O$, cadmium, iron—$FeSO_4.7H_2O$, manganese, chromium—$CrSO_4.7H_2O$, cobalt, and nickel. Ferrous sulphate—$FeSO_4.7H_2O$—is also called "green vitriol" and "copperas." The term "copperas" appears to be a corruption of the French "couperose," which, in turn, is a corruption of the Latin "cuprirosa"—literally "rose of Cyprus." Cyprus was once renowned for its copper mines. The German word for copperas is "vitriol," a term used by Pliny, about 50 A.D. Pliny described this substance as "vitriolus quasi vitrum," meaning "vitriol, a kind of glass," since the crystals resembled green glass, but differed from glass in being easily soluble in water. Sulphuric acid was obtained from "vitriol," and Geber accordingly gave it an Arabic name, which, translated into English, means oil of vitriol. The term "oil" was applied because the acid flows sluggishly like olive oil, and it has an oily feel when rubbed between the fingers (this latter experiment is dangerous).

Ferrous sulphate can be made by dissolving iron in sulphuric acid, and also by exposing iron pyrites (marcasite) to air and moisture. Oxidation occurs, and the liquid which drains away contains iron sulphate and sulphuric acid; the "drainage solution" is converted into ferrous sulphate by the addition of scrap iron; on crystallization, the solution furnishes pale green crystals of ferrous sulphate. Aqueous solutions of the salt oxidize quickly when exposed to the air. The double salt—$FeSO_4.(NH_4)_2SO_4.6H_2O$—ferrous ammonium sulphate, or, Mohr's salt, is employed in volumetric analysis. Its aqueous solution, particularly if acidified with sulphuric acid, oxidizes much more slowly than ferrous sulphate. Ferrous sulphate is used in the manufacture of blue pigments; as a mordant; and in the manufacture of black inks.

Zinc sulphate, $ZnSO_4.7H_2O$.—This salt is very like the magnesium sulphate in its general behaviour. It is made by roasting the native sulphide in air. The zinc sulphate which is formed at the same time is extracted with water—*vide* p. 23. The salt is called "white vitriol." Zinc sulphate is used in making certain battery solutions.

The hydrolysis of zinc and magnesium salts.—Reference might now be made to the hydrolysis of zinc and magnesium chlorides, p. 244. The electrical conductivity of the purest water yet made is very slight, but it can be detected; it is 0.000000038; this number means that a column of water one centimetre long will not conduct an electrical current so well as a column of mercury of equal cross section and extending more than 30 times round the earth. Accordingly, it is inferred that the purest water yet made is slightly ionized: $H_2O \rightleftharpoons H^{\cdot} + OH'$, and that water is

thus an amphoteric oxide Eighteen grams of such water contains about $\frac{1}{10000000}$ of a gram of H ions, and $\frac{17}{10000000}$ of a gram of OH′ ions If all or part of one or other of these two ions be removed, more water molecules will ionize in order to keep the equilibrium value constant The ionization of a few weak acids deduced from conductivity measurements for $\frac{1}{10}$ N-solutions, with HCl as standard of reference, is

Hydrochloric acid	91 400
Carbonic acid	0 174
Hydrosulphuric acid	0 075
Hydrocyanic acid	0 011

Zinc sulphate is completely ionized in dilute solution, $ZnSO_4 \rightleftharpoons Zn + SO_4''$ The Zn ions pair with the OH′ ions of the water to form feebly ionized $Zn(OH)_2$ molecules, more water is ionized in order to maintain the equilibrium value $H_2O \rightleftharpoons H + OH'$, and these actions continue until the concentration of the zinc hydroxide has attained the equilibrium value $Zn(OH)_2 \rightleftharpoons Zn + 2OH'$ When that occurs, a considerable proportion of the OH′ molecules have been withdrawn from the solution to form molecules of zinc hydroxide, and an excess of the H ions in solution are "paired," so to speak, with the SO_4'' ions of the zinc sulphate The scheme may be represented

$$\begin{array}{ccccc} ZnSO_4 & \rightleftharpoons & Zn & + & SO_4'' \\ & & + & & + \\ 2H_2O & \rightleftharpoons & 2OH' & + & 2H \\ & & \updownarrows & & \updownarrows \\ & & Zn(OH)_2 & & H_2SO_4 \end{array}$$

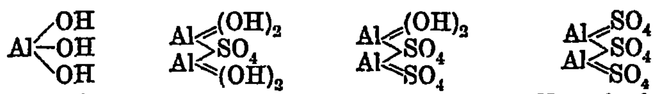
An aqueous solution of zinc sulphate thus behaves in many ways like a solution of sulphuric acid—*e g* turns blue litmus red, etc If an alkali, say sodium hydroxide, be added to the solution of zinc sulphate, the OH′ ions of the base unite directly with the H ions of the acid to form water, and if just sufficient OH′ ions be added to remove all the H ions of the acid, the solution will contain nothing more than would be obtained by dissolving sodium sulphate in water, the zinc hydroxide is removed from the solution by precipitation when its concentration exceeds the solubility coefficient

Lead sulphate, $PbSO_4$—The mineral *anglesite* is the native form of lead sulphate Its rhombic crystals are isomorphous with strontium and barium (not calcium) sulphates It is formed as a white precipitate when sulphuric acid or a soluble sulphate is added to a solution of a lead salt *Vide* p 438 A solution of lead sulphate in sulphuric acid, when boiled, deposits acid lead sulphate—$PbSO_4 \, H_2SO_4 \, H_2O$ Lead sulphate dissolves in hot concentrated hydrochloric acid, in ammonium acetate, and in sodium thiosulphate When potassium sulphate is added to a soluble lead salt, a double lead potassium sulphate, $PbK_2(SO_4)_2$ is formed. The basic lead sulphate $2PbSO_4 \, PbO$ is made commercially by reducing galena with carbon, and subliming the product in a stream of air It is used as a white pigment—*sublimed white lead*—and is not so readily discoloured as white lead.

§ 16 Aluminium Sulphate and the Alums.

Aluminium sulphate, $Al_2(SO_4)_3$.—This salt is prepared by dissolving the hydrated oxide in sulphuric acid. Large quantities too are made by dissolving bauxite, and the purer varieties of clay in the same acid. The crude aluminium sulphate so obtained is called "alum cake," and if much iron is present, "alum ferric cake," used in the purification of sewage. A purer sulphate is made by heating bauxite with sodium carbonate, or by boiling cryolite with milk of lime. In each case a solution of sodium aluminate—$Al_2O_3.3Na_2O$—almost free from iron is obtained. The sodium aluminate is then decomposed by a current of carbon dioxide, and the precipitated aluminium hydroxide is dissolved in sulphuric acid. When the solution is concentrated, the mass solidifies to a white solid which does not crystallize very readily. The crystalline sulphate has the composition represented by $Al_2(SO_4)_3.18H_2O$.

The aqueous solution of aluminium sulphate has an acid reaction, and in the presence of zinc it evolves hydrogen; a basic sulphate is formed at the same time. Obviously, the aluminium sulphate is hydrolyzed in aqueous solution: $Al_2(SO_4)_3 + 6H_2O \rightleftharpoons 2Al(OH)_3 + 3H_2SO_4$. The basic sulphates are formed by boiling the sulphate with freshly precipitated aluminium hydroxide. The composition of the aluminium sulphates—aluminium tervalent—can be represented graphically:



Al hydroxide. Dibasic sulphate. Monobasic sulphate. Normal sulphate.

Werner has another mode of viewing the constitution of the alums which will be described later.

Alums.—When a hot solution of aluminium sulphate is mixed with potassium sulphate, and the solution is cooled, octahedral crystals of a double sulphate of aluminium and potassium separate. The salt has the empirical formula, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, or else $KAl(SO_4)_2.12H_2O$. This salt is a typical member of a large number of isomorphous compounds which are called "alums." Their general formula is

$$R_2^ISO_4.R_2^{III}(SO_4)_3.24H_2O\text{; or, } R^IR^{III}(SO_4)_2.12H_2O$$

where R^I represents an atom of a univalent metal or radicle—potassium, sodium, ammonium, rubidium, cæsium, silver, thallium; and R^{III} represents an atom of a tervalent metal—aluminium, iron, chromium, manganese, thallium. Consequently, an alum is a compound which crystallizes with 12 molecules of water, and is derived from two molecules of sulphuric acid by replacing one hydrogen atom by a univalent atom or radicle; and the remaining three hydrogen atoms by a tervalent metal.

Potash alum	$KAl(SO_4)_2.12H_2O$
Ammonia alum	$NH_4Al(SO_4)_2.12H_2O$
Iron alum	$KFe(SO_4)_2.12H_2O$
Chromium potash alum	$KCr(SO_4)_2.12H_2O$

A series of selenium alums have also been made in which the sulphur atom in K_2SO_4 is replaced by an atom of selenium. The selenium alums are isomorphous with the alums proper.

The alums are usually much more soluble in hot water than in cold, and they are deposited from cooling concentrated solutions of the two salts in the form of octahedral or cubical crystals When heated, the alums give up their water of crystallization Potash alum melts at about 92 5°, and slowly loses all its water of crystallization at 100°, at higher temperatures, the water is driven off more rapidly, and leaves behind a white porous mass called "burnt alum" Ammonia alum when calcined gives a residue of alumina—Al_2O_3—which may contain traces of sulphates The soluble sulphates can be removed by washing

The solubilities and melting points of the alums of the alkali metals are compared in the following scheme

	Sodium	Potassium	Ammonium	Rubidium	Cæsium
Melting point	66°	92 5°	94 5°	105°	120°
Solubility 16°, 100 grams water	51	15	12	2 2	0 6

Lithium does not form a well-defined "alum," and soda alum is not easy to make

Pseudo-alums —A series of double sulphates, sometimes called pseudo-alums, can be made by introducing a bivalent element—manganese, ferrous iron, copper, zinc, magnesium—in place of the univalent element of ordinary alums Thus,

$Al_2(SO_4)_3\ MnSO_4\ 24H_2O$ — Manganese aluminium pseudo alum

$Al_2(SO_4)_3\ FeSO_4\ 24H_2O$ — Ferrous aluminium pseudo alum

These alums are not isomorphous with ordinary alums

Alum-stone or *alunite* is a kind of basic alum—$K_2SO_4\ Al_2(SO_4)_3\ 4Al(OH)_3$—found near Rome, in Hungary, etc It is supposed to have been formed by the action of volcanic sulphur dioxide on the felspathic rocks It is insoluble in water but, on calcination it gives a residuum of alumina (mixed with ferric oxide as impurity) and potash alum passes into solution when the mass is digested with water Alum prepared in this way is called "Roman alum," and that which occurs in commerce is crystallized in cubes Roman alum is fairly free from iron, and it has been in demand—in dyeing, etc —where a specially pure alum is required, but the modern methods of preparation furnish an alum quite as free from iron

Ferric sulphate, $Fe_2(SO_4)_3$ —This salt is prepared by adding sulphuric acid and an oxidizing agent—nitric acid, hydrogen peroxide, etc —to ferrous sulphate Thus, $2FeSO_4 + H_2SO_4 + H_2O_2 = Fe_2(SO_4)_3 + 2H_2O$ On evaporation, a white mass of anhydrous salt, $Fe_2(SO_4)_3$, and some basic sulphate is formed If the solution be mixed with the necessary amount of potassium sulphate, violet octahedral crystals of iron alum, mentioned above, separate

§ 17 Persulphuric Acid and the Persulphates

M. Berthelot (1878) found that when a mixture of oxygen and sulphur dioxide is exposed to the silent discharge in an ozone tube, oily drops of sulphur heptoxide, S_2O_7, are formed $2SO_2 + O_3 = S_2O_7$ The liquid forms white crystals at 0° It gradually decomposes, on keeping, into sulphur trioxide and oxygen Sulphur heptoxide combines with water with a hissing noise like sulphur trioxide, but the solution has not the same properties as if sulphur trioxide alone had been dissolved in the water A similar solution can be obtained by mixing concentrated sulphuric acid

with hydrogen peroxide in the cold, and by the electrolysis of concentrated sulphuric acid

The preparation of persulphates.—It will be remembered that when dilute sulphuric acid is electrolyzed, hydrogen and oxygen are obtained in the proportion 2 volumes of hydrogen, and one volume of oxygen. As the concentration of the acid is increased, less and less oxygen is evolved, until, with 50 per cent. sulphuric acid and a cold solution, inappreciable quantities of oxygen will be disengaged at the anode. A new compound is formed—persulphuric acid, $H_2S_2O_8$. The best way of studying this action is to electrolyze a saturated solution of potassium sulphate in sulphuric acid, specific gravity about 1.3

The solution is placed in a test-tube, *A*, Fig 169, so that the test tube is about three fourths filled. The test-tube is fixed in a large beaker by means of the wire *C*. A glass cylinder *D*, is fixed in the test tube by means of the wire *B*. A coil of platinum wire—the cathode—is allowed to dip into the solution of potassium sulphate as indicated in the diagram and a platinum wire sealed to a piece of glass tube so that about 1½ to 2 cm of the wire projects from the tube forms the anode. This is fixed within the cylinder. The large beaker is filled with water in which pieces of ice are floating—"iced water." A current of about one or two amperes is sent through the solution. Hydrogen appears at the cathode, and a white crystalline mass accumulates at the anode. In about 45 minutes the current may be stopped, the white crystals of potassium persulphate collects on a filter paper, wash with alcohol, and finally with ether.

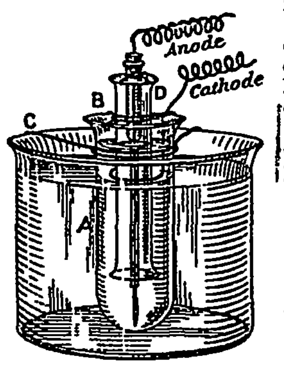


FIG 169.—Preparation of Potassium Persulphate

The formula $K_2S_2O_8$ is conformable with the change in the molecular conductivity of solutions of the salt with dilution, and with the lowering of the freezing point of solutions of the salt. H Marshall, who first isolated potassium persulphate in 1891, suggested the formula KSO_4, but later favoured the doubled formula given above.

The properties of persulphates.—The solid persulphates are fairly stable. Potassium persulphate decomposes on heating into potassium pyrosulphate and oxygen: $2K_2S_2O_8 = 2K_2S_2O_7 + O_2$. An aqueous solution of a persulphate is a powerful oxidizing agent, and is used for that purpose in analytical work, *e.g.* it precipitates a brown manganese peroxide from soluble manganese salts. The persulphates *slowly* liberate iodine from solutions of potassium iodide, oxidize iodine to iodic acid, etc. A solution of a manganese salt gives a precipitate of manganese peroxide with potassium persulphate, but, in the presence of silver nitrate, is oxidized to pink permanganate—*Marshall's reaction*. The intensity of the coloration is proportional to the amount of manganese present, and hence, the reaction is utilized for the colorimetric determination of manganese. Unlike hydrogen peroxide, the persulphates do not give orange yellow colorations with titanium salts. Most of the persulphates are soluble. Barium persulphate is readily soluble in water. Hence barium chloride gives no precipitate with the persulphates, although it does give a precipitate with a sulphate, but if the persulphate be decomposed by warming, a precipitate of barium sulphate is obtained. A dilute solution of the acid—persulphuric acid, also called perdisulphuric acid—can be made

by treating the barium persulphate with sulphuric acid The persulphates are used in photography for "reducing" negatives, and ammonium persulphate is used in technical organic chemistry.

Caro's acid—If potassium persulphate be digested with 40 per cent sulphuric acid in a freezing mixture so that there is no rise of temperature, or if concentrated sulphuric acid and hydrogen peroxide (5 per cent) be mixed together, a permonosulphuric acid is obtained $H_2SO_4 + H_2O_2 \rightleftharpoons H_2O + H_2SO_5$ The solution is sometimes called Caro's acid, H_2SO_5—after its discoverer, N Caro, 1898 An acid, 92 3 per cent purity, has been made by the action of pure hydrogen peroxide on sulphur trioxide $H_2O_2 + SO_3 = H_2SO_5$ The pure acid forms a white crystalline mass, which melts at about 45°, and it is comparatively stable Like persulphuric acid, Caro's acid has strong oxidizing qualities Unlike persulphuric acid, it liberates iodine from potassium iodide *at once* It also oxidizes sulphur dioxide to the trioxide, ferrous salts to ferric salts, and precipitates peroxides from salts of silver, copper, manganese, cobalt, and nickel It does not bleach permanganates, nor oxidize chromic nor titanium salts, and is therefore distinct from hydrogen peroxide The relations of the two acids with pyro- or di sulphuric acid, will appear from the supposed graphic formulæ

$$\underset{\text{Disulphuric acid}}{O\begin{matrix}\diagup SO_2.OH \\ \diagdown SO_2.OH\end{matrix}} \qquad \underset{\text{Perdisulphuric acid}}{\begin{matrix}O—SO_2.OH \\ O—SO_2.OH\end{matrix}} \qquad \underset{\text{Caro's acid}}{\begin{matrix}O—SO_2.OH \\ OH\end{matrix}}$$

Persulphuric acid is accordingly sometimes called perdisulphuric acid to distinguish it from "permonosulphuric acid" or Caro's acid Another scheme brings out the relation of these persulphuric acids to hydrogen peroxide

$$\underset{\text{Hydrogen peroxide}}{\begin{matrix}O—H \\ O—H\end{matrix}} \qquad \underset{\text{Caro's acid}}{\begin{matrix}O—SO_2—OH \\ O—H\end{matrix}} \qquad \underset{\text{Persulphuric acid}}{\begin{matrix}O—SO_2—OH \\ O—SO_2—OH\end{matrix}} \qquad \underset{\text{Sulphur heptoxide}}{\begin{matrix}O—SO_2 \\ O—SO_2\end{matrix}>O}$$

There has been some discussion whether Caro's acid is monobasic, H_2SO_5, or dibasic, $H_2S_2O_9$ The analysis of the potassium salt is not conclusive, since $KHSO_5$ would have the same ultimate composition as the salt $K_2S_2O_9.H_2O$ Benzoyl chloride, $C_6H_5.CO.Cl$, reacts with the potassium salt of Caro's acid, forming the benzoyl derivative This reaction undoubtedly corresponds with the monobasicity of the acid

$$\begin{matrix}O—SO_2OK \\ O—H\end{matrix} + C_6H_5.CO.Cl = HCl + \begin{matrix}O—SO_2OK \\ O—CO.C_6H_5\end{matrix}$$

It is very unlikely that this result would occur if the formula of the salt in question were $K_2S_2O_9.H_2O$ The synthesis of Caro's acid by the action of the calculated quantity of chlorosulphonic acid, $SO_2Cl(OH)$, on pure hydrogen peroxide in the cold

$$\begin{matrix}SO_2OH \\ Cl\end{matrix} + H_2O_2 = HCl + \begin{matrix}O—SO_2OH \\ O—H\end{matrix}$$

is in agreement with the view of the molecular formula just indicated

Persulphuric acid—If Caro's acid be mixed with the calculated quantity of chlorosulphonic acid, crystals of persulphuric acid are formed

$$\begin{matrix} O-SO_2OH \\ O-H \end{matrix} + \begin{matrix} Cl \\ SO_2OH \end{matrix} = HCl + \begin{matrix} O-SO_2OH \\ O-SO_2OH \end{matrix}$$

The hydrogen chloride is removed by keeping the mixture in a desiccator under reduced pressure. The white crystalline mass so obtained is more stable than Caro's acid. It melts just above 60° with decomposition. The aqueous solution is first hydrolyzed into Caro's acid and sulphuric acid $H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4$, and then decomposes into oxygen and sulphuric acid $2H_2S_2O_8 + 2H_2O = 4H_2SO_4 + O_2$. In consequence, the pure acid cannot be prepared by treating the persulphates with dilute acids, as indicated above, and then concentrating the solution. When sodium or potassium persulphate is exposed to the action of sulphur trioxide vapour two molecules of the latter unite with one molecule of the former producing potassium perpyrosulphate, $KS_2O_6 O_2 S_2O_6K$

Persulphate	Pyrosulphate	Perpyrosulphate
$\begin{matrix} O-SO_2OK \\ O-SO_2OK \end{matrix}$	$O\!<\!\begin{matrix} SO_2OK \\ SO_2OK \end{matrix}$	$\begin{matrix} O-O\,SO_2\,O\,SO_2OK \\ O-O\,SO_2\,O\,SO_2OK \end{matrix}$

§ 18 Thiosulphuric Acid and the Thiosulphates

Preparation—If an aqueous solution of sodium sulphite, Na_2SO_3, be exposed to the air, one oxygen atom per molecule of sodium sulphite is taken up, and sodium sulphate, Na_2SO_4, is formed $2Na_2SO_3 + O_2 = 2Na_2SO_4$. Similarly, if sodium sulphite be digested with finely divided sulphur for some time, one atom of sulphur per molecule of sodium sulphite is taken up, and a new salt, sodium thiosulphate, $Na_2S_2O_3$, is formed $Na_2SO_3 + S = Na_2S_2O_3$. These reactions suggest some analogy in the structure of the thiosulphates and the sulphates, and this is emphasized by the term *thio* sulphates, i.e. *sulpho* sulphates—from the Greek θεῖον (theion), sulphur

Sodium thiosulphate is also formed when a mixture of sodium sulphide and sulphite is treated with iodine. $Na_2S + Na_2SO_3 + I_2 = Na_2S_2O_3 + 2NaI$. This reaction is sometimes supposed to occur in two steps: $Na_2S + I_2 = 2NaI + S$, and the liberated sulphur acts upon the sodium sulphite as indicated above. The net result of the reaction is that the iodine withdraws one atom of sodium from the molecule of sodium sulphide and one from the sodium sulphite, while the residues unite to form a more complex molecule condensation product. This operation is sometimes called Spring's reaction—after W. Spring's syntheses of the thionic acids by this reaction in 1874

$$\begin{matrix} S\!<\!\begin{matrix} Na \\ Na \end{matrix} \\ SO_3\!<\!\begin{matrix} Na \\ ONa \end{matrix} \end{matrix} + I_2 = 2NaI + SO_2\!<\!\begin{matrix} SNa \\ ONa \end{matrix}$$

The thiosulphates are also formed by the action of sodium sulphide—Na_2S or Na_2S_2—upon sulphur dioxide. Some sulphur separates at the same time $2Na_2S + 3SO_2 = 2Na_2S_2O_3 + S$. The action is supposed to

occur in three steps (1) formation of sodium sulphite and hydrogen sulphide: $SO_2 + H_2O + Na_2S = Na_2SO_3 + H_2S$; (2) the hydrogen sulphide reacts with the sulphur dioxide, as indicated on p 414, liberating free sulphur $SO_2 + 2H_2S = 2H_2O + 3S$, and (3) the liberated sulphur is taken up by the sodium sulphite as indicated above By boiling sulphur with milk of lime or with sodium hydroxide, a mixture of the corresponding thiosulphate and sulphide is formed, *e.g* $3Ca(OH)_2 + 12S = CaS_2O_3 + 2CaS_5 + 3H_2O$ The calcium sulphide is converted into the thiosulphate on oxidation by exposure to the air $2CaS_5 + 3O_2 = 6S + 2CaS_2O_3$. When the "tank waste" of Leblanc's process (*q v*) is exposed to the air, the calcium sulphide, CaS, is in part transformed into calcium thiosulphate, CaS_2O_3, the latter, when treated with sodium carbonate forms insoluble calcium carbonate, and soluble sodium thiosulphate $CaS_2O_3 + Na_2CO_3 = Na_2S_2O_3 + CaCO_3$

Thiosulphuric acid.—Thiosulphuric acid has not been isolated. By acting on a thiosulphate with a mineral acid, thiosulphuric acid appears to be formed, but it begins to decompose at once into sulphur dioxide and free sulphur $Na_2S_2O_3 + 2HCl = 2NaCl + H_2O + SO_2 + S$ The sulphur only appears after the elapse of a certain time—seconds or minutes, according to the concentration of the solution It has been stated that the decomposition of the thiosulphate does not occur at once If, however, the acidified solution be neutralized before the turbidity appears, the neutralization does not stop the separation of the sulphur Some thiosulphuric acid must therefore have decomposed. Probably the very finely divided sulphur is not visible until the fine particles have clotted into larger granules. The evolution of sulphur dioxide with the separation of sulphur on the addition of a dilute mineral acid, distinguishes thiosulphates from sulphites in qualitative analysis.

Properties and uses of thiosulphates.—Sodium thiosulphate is the most important salt of thiosulphuric acid, and it is called, by photographers sodium hyposulphite, or simply "hypo" This salt is readily soluble in water, and the aqueous solution readily dissolves silver chloride, bromide, or iodide A soluble silver sodium thiosulphate is formed $2AgCl + 3Na_2S_2O_3 \rightleftharpoons NaCl + Ag_2Na_4(S_2O_3)_3$ Hence its use in the "fixing bath" of the photographer

Sodium thiosulphate is readily oxidized by potassium permanganate, nitric acid, chlorine, etc It is used in preference to sulphurous acid (*q v*) as an "antichlor" in order to remove the last trace of chlorine from the bleached goods The action depends upon the oxidizing qualities of sodium thiosulphate $Na_2S_2O_3 + 5H_2O + 4Cl_2 = Na_2SO_4 + H_2SO_4 + 8HCl$, or $Na_2S_2O_3 + H_2O + Cl_2 = Na_2SO_4 + 2HCl + S$. Sodium thiosulphate is reduced by sodium amalgam reforming sodium sulphide and sulphite $Na_2S_2O_3 + 2Na = Na_2SO_3 + Na_2S$

Solutions of iodine are quickly decolorized by sodium thiosulphate with the formation of sodium tetrathionate, $Na_2S_4O_6$ Thus, $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$. If a solution of sodium thiosulphate of known strength be added from a burette to a solution containing some iodine, until the colour of the iodine has just disappeared the amount of thiosulphate required for the work of decolorization furnishes the datum necessary for calculating the amount of iodine in the given solution

Sodium thiosulphate crystallizes in large transparent monoclinic prisms

with five molecules of water of crystallization $Na_2S_2O_3 \cdot 5H_2O$, the phenomenon of undercooling exhibited by this salt, has been previously discussed

Constitution of thiosulphates.—It is not very clear whether thiosulphuric acid, and accordingly also the thiosulphates, should be represented by graphic formula based on

$$\begin{matrix} O \\ S \end{matrix} \!\!\geqslant\! S \!<\! \begin{matrix} OH \\ OH \end{matrix}, \quad \text{or} \quad \begin{matrix} O \\ O \end{matrix} \!\!\geqslant\! S \!<\! \begin{matrix} SH \\ OH \end{matrix}$$

Some prefer the latter, others the former, and some consider that both varieties exist The former is then called symmetrical, and the latter asymmetrical thiosulphuric acid. The available evidence, however, favours the asymmetrical $HS \cdot SO_2 \cdot OH$.

§ 19 Polythionic Acids

There is a remarkable series of five acids—called collectively the polythionic acids—closely related to sulphurous acid and to thiosulphuric acid. The polythionic acids include di-, tri-, tetra-, penta-, and hexathionic acids To show C W Blomstrand's (1869) and D I. Mendeléeff's (1870) views of the inter relations of the polythionic acids it is convenient to consider the group SO_2OH—i.e. $\begin{matrix} O \\ O \end{matrix} \!\!\geqslant\! S \!<\! {}^{OH}$ as a monad radicle The constitution of the thionic acids is then represented by the following graphic formulæ—with hydrogen H—H as the starting point

$\begin{matrix} SO_2OH \\ H \end{matrix}$	$\begin{matrix} SO_2OH \\ SO_2OH \end{matrix}$	$S \!<\! \begin{matrix} SO_2OH \\ SO_2OH \end{matrix}$	$S \!<\! \begin{matrix} S{-}SO_2OH \\ SO_2OH \end{matrix}$	$S \!<\! \begin{matrix} S{-}SO_2OH \\ S{-}SO_2OH \end{matrix}$
Sulphurous acid	Dithionic acid	Trithionic acid	Tetrathionic acid	Pentathionic acid

We previously encountered this curious faculty of sulphur, whereby "chains of atoms" can be linked together, in our study of the hydrogen sulphides From this point of view pentathionic acid is related to hydrogen trisulphide tetrathionic acid to hydrogen persulphide, and trithionic acid and thiosulphuric acid are related to hydrogen monosulphide as follows

$S \!<\! \begin{matrix} H \\ H \end{matrix}$	$S \!<\! \begin{matrix} H \\ SO_2OH \end{matrix}$	$S \!<\! \begin{matrix} SO_2OH \\ SO_2OH \end{matrix}$
Hydrogen monosulphide	Thiosulphuric acid	Trithionic acid

It is interesting to compare the latter with pyrosulphuric acid, persulphuric acid, and Caro's acid previously discussed, since in these compounds, oxygen takes the place of sulphur There are other modes of interpreting the known properties of these acids, but Blomstrand's views, just indicated agree best with more recent observations

Dithionic acid, $H_2S_2O_6$.—The sodium salt is made together with some sulphuric acid, by Spring's reaction with iodine on sodium sulphite

$$\begin{matrix} SO_2 \!<\! \begin{matrix} ONa \\ Na \end{matrix} \\ SO_2 \!<\! \begin{matrix} Na \\ ONa \end{matrix} \end{matrix} + I_2 = 2NaI + \begin{matrix} SO_2{-}ONa \\ | \\ SO_2{-}ONa \end{matrix}$$

Dithionic acid has been called "hyposulphuric acid," and the salts, "hyposulphates" The manganese salt, MnS_2O_6, is made by passing sulphur

dioxide through water with manganese dioxide in suspension $MnO_2 + 2SO_2 = MnS_2O_6$ At the same time there is a side reaction between the manganese dithionate and the manganese dioxide $MnO_2 + MnS_2O_6 = 2MnSO_4$ This reduces the yield The manganese salt is converted into barium dithionate, BaS_2O_6, by mixing it with barium hydroxide, $Ba(OH)_2$, and the resulting salt can be purified by crystallization $BaS_2O_6 \, 2H_2O$ is formed This gives soluble dithionic acid and insoluble barium sulphate when treated with dilute sulphuric acid The aqueous solution of the acid can be concentrated by evaporation until its specific gravity is about 1 35, any further concentration decomposes the acid $H_2S_2O_6 = SO_2 + H_2SO_4$ If the sodium dithionate be reduced in aqueous solution by means of sodium amalgam, sodium sulphite is reformed $Na_2S_2O_6 + 2Na = 2Na_2SO_3$

Trithionic acid, $H_2S_3O_6$—The sodium salt of this acid is formed by passing sulphur dioxide through a concentrated solution of potassium thiosulphate $3SO_2 + 2K_2S_2O_3 = S + 2K_2S_3O_6$ There is some doubt if Spring's reaction, the action of iodine upon a mixed solution of sodium sulphite and thiosulphate, proceeds

$$\begin{matrix} SO_2<^{ONa}_{Na} \\ SO_2<^{S.Na}_{ONa} \end{matrix} + I_2 = 2NaI + \begin{matrix} SO_2\text{—}ONa \\ | \\ S \\ | \\ SO_2\text{—}ONa \end{matrix}$$

as might be expected, because a mixture of the sulphate and tetrathionate is obtained Sodium trithionate is also formed by the action of sulphur chloride, SCl_2, upon sodium sulphite, and by warming an aqueous solution of potassium acid sulphite with flowers of sulphur $6KHSO_3 + 2S = 2K_2S_3O_6 + K_2S_2O_3 + 3H_2O$ By boiling silver thiosulphate with water, a molecule of Ag_2S splits from two molecules of the thiosulphate and silver trithionate remains The acid itself is formed from the potassium salt by the addition of hydrofluosilicic acid. Potassium fluosilicate is precipitated, and the trithionic acid remains in solution The acid and its salts are readily decomposed into sulphur, and sulphuric acid or a sulphate By the reducing action of sodium amalgam, sodium trithionate is converted back into sodium sulphite and sodium thiosulphate

Tetrathionic acid, $H_2S_4O_6$—The sodium salt is formed by Spring's reaction with iodine and sodium thiosulphate

$$\begin{matrix} NaO\text{—}SO_2\text{—}S\,Na \\ NaO\text{—}SO_2\text{—}S\,Na \end{matrix} + I_2 = 2NaI + \begin{matrix} NaO\text{—}SO_2\text{—}S \\ NaO\text{—}SO_2\text{—}S \end{matrix}$$

The barium salt is prepared in a similar manner, and from this the acid itself is obtained by the action of dilute sulphuric acid The reaction under consideration is the last of the set of condensations by the removal of an atom of sodium from each of two molecules of a salt and the condensation of the residues to form a more complex molecule—with sodium thiosulphate, di-, (tri-), and tetrathionate All these reactions are reversed and the original salts reproduced by treating the complex salts with sodium amalgam As indicated above, the reaction between iodine and sodium thiosulphate is much utilized in volumetric analysis for the quantitative determination of iodine

Pentathionic acid, $H_2S_5O_6$—When hydrogen sulphide is passed into

a solution of sodium tetrathionate, the salt decomposes and nascent sulphur is probably formed $Na_2S_4O_6 + 5H_2S = 2NaOH + 4H_2O + 9S$. The nascent sulphur then unites with the undecomposed tetrathionate, forming sodium pentathionate $Na_2S_4O_6 + S = Na_2S_5O_6$ The same salt is formed, more or less contaminated with trithionate, when a solution of the tetrathionate decomposes $2Na_2S_4O_6 = Na_2S_3O_6 + Na_2S_5O_6$, and it is also formed by the action of sulphur monochloride, S_2Cl_2, on barium thiosulphate

$$2SO_2<\begin{matrix}O\\S\end{matrix}>Ba + S_2Cl_2 = S + BaCl_2 + S<\begin{matrix}S\,SO_2\,O\\S\,SO_2\,O\end{matrix}>Ba$$

When hydrogen sulphide is passed into a concentrated solution of sulphurous acid at 0°, a solution containing a number of the polythionic acid is formed It is called **Wackenroder's solution** It is probable that the first action of the hydrogen sulphide results in the formation of tetrathionic acid $H_2S + 3SO_2 = H_2S_4O_6$, and that this decomposes into the tri and pentathionic acids as indicated above[1] The passage of the hydrogen sulphide can be continued until the solution contains little more [illegible] sulphur and pentathionic acid The solution containing the p[illegible] polythi[illegible]acid can be concentrated by evaporation until it [illegible]pecific gravi[illegible] about 1 46, and then saturated with potassium hydro[illegible] the solution is filtered to remove the sulphur and allowed to c[illegible] monad tancously The crystals which separate have the empirical [illegible] $K_2S_5O_6\,3H_2O$ The final products of the action are sulphur [illegible] by the $H_2S_5O_6 + 5H_2S = 6H_2O + 10S$, or $SO_2 + 2H_2S = 3S$ [illegible] point pentathionates give a brown precip[illegible] $S<\begin{matrix}S—SO_2OH\\[illegible]\end{matrix}$ $S<\begin{matrix}S—SO_2OH\\S—SO_2OH\end{matrix}$ solutions The precipitate soon beco[illegible] the pentathionates give an immedia[illegible] precipitate of sulphur

Potassium hexathionate, $K_2S_6O_6$, corresponding with the unknown **hexathionic acid**, $H_2S_6O_6$, is said to have been prepared in an impure condition from the mother liquid remaining after the separation of potassium pentathionate The aqueous solution is very unstable It reacts like the pentathionates with potassium hydroxide and ammoniacal silver nitrate, but it gives an *immediate* precipitate of sulphur with ammonia, the pentathionates give a precipitate with ammonia on standing a short time

✓ **General properties**—Aqueous solutions of all the acids decompose when the attempt is made concentrate them $H_2S_nO_6 = H_2SO_4 + SO_2 + (n-2)S$, the solid salts decompose in a similar manner when heated In dithionic acid, $n = 2$, and this corresponds with the fact that aqueous solutions of this acid yield no sulphur on decomposition, the other polythionic acids decompose with the separation of sulphur Tetrathionic acid seems to be the most stable acid of the series. The barium salts are all soluble in water The aqueous solutions of the alkaline polythionates decompose slowly Mercurous nitrate gives no precipitate with dithionic acid, a black precipitate with trithionic acid and yellow precipitates with tetra and pentathionic acids Potassium hydroxide gives a precipitate of sulphur with pentathionic acid, and no precipitate with the other acids, dilute hydrochloric acid gives a precipitate of sulphur and evolution of

[1] According to H Debus Wackenroder's solution contains a soluble form of S which separates as an amorphous gelatinous mass which is said to be a hydrated form of sulphur, $S_8\,nH_2O$

sulphur dioxide with trithionic acid, and with the other acids no change is observed

History —Dithionic acid was discovered by J J Welter and J L Gay-Lussac in 1819, trithionic acid, by C Langlois in 1842, tetrathionic acid, by M. J Fordos and A Gelis, 1843, and pentathionic acid by H W F Wackenroder in 1845 The latter was specially studied by H Debus in 1888 Thiosulphates were made by F Chaussier in 1799, and afterwards carefully studied by L N Vauquelin in 1800

§ 20 Review of the Oxides and Oxyacids of Sulphur

We may now tabulate the list of the oxides and oxyacids of sulphur discussed in what precedes

Oxides		Acids	
[Sulphur monoxide	SO]	[Sulphoxylic acid	H_2SO_2]
Sulphur sesquioxide	S_2O_3	Hyposulphurous acid	$H_2S_2O_4$
Sulphur dioxide	SO_2	Sulphurous acid	H_2SO_3
Sulphur trioxide	SO_3	Sulphuric acid	H_2SO_4
		Pyrosulphuric acid	$H_2S_2O_7$
Sulphur heptoxide	S_2O_7	Persulphuric acid	$H_2S_2O_8$
		Caro's acid	[illegible]SO_5
—		Thiosulphuric acid	[illegible]$_3$
—		Dithionic acid	[illegible]O_6
—		Trithionic acid	[illegible]S_3O_6
—		Tetrathionic acid	$H_2S_4O_6$
—		Pentathionic acid	$H_2S_5O_6$
—		[Hexathionic acid]	$H_2S_6O_6$

Sulphoxyl[illegible] upon sodium sulph[illegible] known in the form of an organic derivative disc[illegible] organic chemistry Sulphur monoxide, SO, is un[illegible]nown The sul[illegible]ones, $R_2'SO_2$, and the sulphinic acids, R' SO OH, of organic chemis[illegible], are related to the unknown sulphoxylic acid, H_2SO_2

§ 21 Nascent Action

We have just alluded to the action of "nascent" sulphur, and some other examples of nascent action have been previously encountered, pp 103, 239 Ordinary free hydrogen, oxygen, chlorine, etc, are unable to affect many substances which are readily attacked by mixtures known to yield hydrogen, oxygen, chlorine, etc An element at the moment of its separation appears to be more chemically active than after it has been made a few moments Amongst the various hypotheses which have been suggested, three are plausible explanations of the phenomenon

1 Atomic hypothesis —Here it is assumed that nascent hydrogen is in the atomic condition and does its work before the atoms have had time to form ordinary molecules There is, however, no direct evidence that, say, atomic hydrogen ever has a separate existence during the reaction (p 292)

2 Ionic hypothesis —It will be remembered that the action of hydrochloric acid upon zinc, according to the ionic hypothesis, involves little more than the transfer of two positive charges from the hydrogen ion to the zinc atom $Zn + 2H^{\cdot} + 2Cl' = Zn^{\cdot\cdot} + 2Cl' + H_2$, and nascent hydrogen thus represents the condition of the element at the instant when its ions give up their electric charges

3 Energy hypothesis —During the reaction between, hydrochloric acid, energy is running down in the form of $2HCl + Aq \rightarrow 2ZnCl_2 + H_2 + Aq + 112.8$ Cals The gr of nascent hydrogen is ascribed to the energy of the r available for inaugurating another reaction rather than b away as heat 202)

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§ 22 Selenium and Tellurium

The elements selenium and tellurium cannot be class common elements. They are not very abundantly dis ion of ' half mile crust " of the earth Small quantities of se poly- found associated with sulphur and the sulphides, e.g It is selenium is found in the " flue dust " of the " pyri the the manufacture of sulphuric acid Small quantities c this found associated with gold, silver and bismuth ores. The recognized by the early mineralogists, and Muller von Rei is 1782, considered it to be a new element, which M H Klapr g n ed tellurium—from the Latin *tellus*, the earth Selenium covered by J J Berzelius, in 1817, and named selenium, from σελήνη (selēnē), the moon, owing to its resemblance to tellurium a few years before

Tellurium is a silver grey solid with a metallic lustre, sel reddish brown powder Like sulphur, both elements exist allotropic forms, but the allotropism of tellurium is less marke selenium Both elements conduct electricity, although one selenium is almost a non conductor Both elements form compounds—H_2Se and H_2Te—corresponding with hydrogen These compounds are all prepared in a similar manner, and th tively precipitate selenides and tellurides from solutions of sal metals Hydrogen telluride is unstable even below 0°, hydroger is rather more stable, but it decomposes in the light

The two elements are monatomic at 2000° Both elements bu air with a blue flame, forming dioxides—SeO_2 and TeO_2—analogous sulphur dioxide The dioxides dissolve in water forming solutions a gous with sulphurous acid, and these, on oxidation, give seleni telluric acids, which, in turn, form selenates and tellurates ana with the sulphates Selenic acid is weaker than sulphuric acid telluric acid is weaker than selenic acid The two elements also fo chlorides and bromides analogous with the corresponding sulphur chlorid and bromides

Selenium is used to a small extent in the production of certain ro and red colours for glass and enamels, and also for " bleaching," that neutralizing, the green tinge of glass Perhaps the most interest property of selenium is the decrease which occurs in its electrical co ductivity or the increase in its electrical resistance on exposure to light- discovered by W Smith (1873) The change is proportional to t intensity of the light, red and orange light are the most active T phenomenon is illustrated by the curve, Fig 169A, where the electric resistance of selenium is plotted on passing from light to darkness a back to light again The change after exposure is not instantaneo

sulphur dio kness the selenium takes a little time to recover its normal is observed Siemens (1875) supposed that the phenomenon depended upon History - of selenium from a feeble conducting variety a selenium, to a Gay-Lussac icting variety β selenium, both forms assume a condition of thionic acid, in light and in darkness, but in light the equi—brium is displaced by H W F of the more conducting variety, and this the ore the greater H Debus inty of the light

and afterwar ⇌β Selenium
<—Darkness

§ 20 hange is ac- We may no he presence discussed in wl inum, etc, 3 catalytic O interesting [Sulphur mon have been Sulphur sesc curious phe- Sulphur dious e g telephoto- Sulphur tri eless telephony, Sulphur he y, automatic con- supply of gas in illuminated buoys, etc

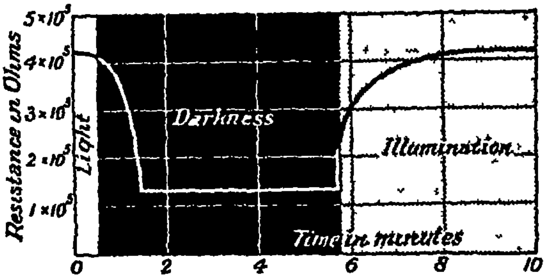


Fig 169A —The Effect of Light and Darkness on the Electrical Resistance of Selenium

§ 23 The Oxygen Family of Elements

Sulpho n, sulphur, selenium, and tellurium form an interesting group derivative ts The relationship is not so clearly defined as with the halogens oxide, S(upare oxygen with tellurium, it would require some imagination acids, R the relationship significant, but on comparing any one element sulphoxy neighbour in the series O, S, Se, Te, the relationship becomes nphatic. They are all bivalent The physical properties are mpared in the form of a table which brings out the gradation in operties very clearly For instance, the specific gravities, melting p nts, boiling points, etc, increase with increasing atomic weight Oxygen t one end of the series, tellurium at the other

Table XXIX —Properties of the Oxygen Sulphur Family

	Oxygen	Sulphur	Selenium	Tellurium
mic weight	16	32 07	79 2	127 5
ting point	−227°	114°–115°	170°–217°	452°–454°
ling point	−183°	448°	688°	1390°
cific gravity (solid)	1 43	1 96–2 06	4 28–4 80	5 93–6 4
mic volume (approx)	11	16	18	21
ur of solid	Pale blue	Yellow	Reddish brown	Black
t of union with hy-rogen (cals)	69 0	4 8	−25 1	−34 9

Selenium, and tellurium particularly, lie very close to that ill defined

border line between the metals and non metals All four elements exhibit allotropism Oxygen occurs most abundantly, sulphur next, and tellurium least They all produce hydrogen compounds of the same type, but while the hydrogen compounds of sulphur, selenium, and tellurium are fœtid smelling gases at ordinary temperatures, hydrogen oxide, H_2O, is a colourless, odourless liquid The acidic character of the hydrides increases with increasing atomic weight Tabulating the properties of the hydrides analogous with water, we get

TABLE XXX —PROPERTIES OF THE HYDRIDES OF THE SULPHUR OXYGEN FAMILY

Symbol	Molecular weight	Boiling point	Melting point.	Specific gravity	Dissociation temperature	Reaction (litmus)
H_2O	18 02	100°	0°	1	1800°	Neutral
H_2S	34 09	−61 8°	−85 5°	1 17	400°	Acid
H_2Se	81 22	−42°	−64°	2 81	150°	Acid
H_2Te	129 52	0°	−48°	2 57	0°	Acid

The first two also form H_2O_2 and H_2S_2 respectively Sulphur, selenium, and tellurium unite with oxygen to form trioxides, but they do not form similar compounds with one another The dioxides, however, form an interesting set if we regard ozone as an oxygen dioxide, thus

$$O{<}^{O}_{O} \qquad S{<}^{O}_{O} \qquad Se{<}^{O}_{O} \qquad Te{<}^{O}_{O}$$

Oxygen dioxide Sulphur dioxide Selenium dioxide Tellurium dioxide

Of course, the graphic formulæ could here have been given with oxygen, sulphur, etc , quadrivalent The analogy between ozonic acid $(HO)_2O$ O and sulphurous acid $(HO)_2S$ O might also be cited

Tellurium dioxide is an "intermediate oxide," because it acts both as an acid and as a base (p 144)—thus, tellurium sulphate, $Te(SO_4)_2$ is known, and yet tellurous acid, H_2TeO_3, like sulphurous acid, forms salts called tellurites, *e.g* K_2TeO_3, $KHTeO_3$, etc The remarkable number of compounds of the metals with oxygen and sulphur, and the similarity in the constitution of the compounds of sulphur and of oxygen, has already been emphasized Tellurium and selenium have not been so closely studied as sulphur and oxygen, but they undoubtedly show a similar behaviour in a less marked degree All three form trioxides SO_3, SeO_3, and TeO_3 All four elements form halides, although there are some gaps

OH_2,	S_2Cl_2,	Se_2Br_2,	—
OCl_2,	SCl_2,	—,	$TeCl_2$,
—,	SCl_4,	$SeCl_4$,	$TeCl_4$,
—,	SF_6,	SeF_6,	TeF_6, *etc*

All four elements form compounds of the type of sulphides

$$OAg_2, \qquad SAg_2, \qquad SeAg_2, \qquad TeAg_2,$$

Questions

1 Give a brief account of the manufacture of strong sulphuric acid What are the three most common impurities in the concentrated acid ? How may they be detected and removed ?—*London Univ*

2 Sulphuric acid is said to be dibasic, and to contain in its molecule two hydroxyl groups, on what evidence are these statements made ? What is the origin of the name "oil of vitriol" by which this acid is known in commerce ? —*London Univ*

Discuss the acids formed by the solution of SO_2 and SO_3 in water What is a sulphonic acid ?—*Owens Coll*

3 Explain exactly the meaning of the formula SO_2 Describe how the composition of this gas may be determined —*Aberdeen Univ*

4 Explain the meaning of the underlined words —" The *anhydrous, neutral salt, insoluble* in *aqueous solvents,* was *decomposed* by an *equivalent* quantity of *dibasic acid,* producing some *gaseous anhydride* and a *saturated solution* of an *inorganic* salt without *water of crystallization* but very *deliquescent* "—*Dartmouth Coll, U S A*

5 Give some examples of chemical changes which take place slowly Have any observations been made between the rate and the condition of such change ?—*New Zealand Univ*

6 Describe the means you would adopt in order to prepare from sodium sulphite (*a*) sodium hyposulphite and (*b*) sodium thiosulphate Discuss the existing evidence concerning the constitution of each of these three compounds —*Science and Art Dept*

7 Calculate the volume of a solution of sulphuric acid, density 1 8 and containing 89 per cent of pure acid, that would be required to make 200 grams of hydrochloric acid by acting on sodium chloride Atomic weights —$H = 1$, $S = 32$, $O = 16$, $Na = 23$ $Cl = 35\ 5$) —*Sheffield Scientific School, U S A*

8 Why does sulphuric acid become hot when a limited amount of cold water is added to it ? In what proportion is water added to produce the greatest heat ? —*Amherst Coll, U S A*

9 With sulphuric acid as the example, explain the meaning you attach to the terms "acid" and "dibasic acid" What is the behaviour towards litmus of $NaHCO_3$, Na_2CO_3, $NaHSO_4$, Na_2SO_4, and how do you account for it ?—*Sheffield Univ*

10 —(*a*) Why is sodium sulphate not utilized as a source of sulphuric acid, as sodium chloride is for hydrochloric acid ?

(*b*) Describe briefly the manufacture of sulphuric acid by the "Contact Process"

(*c*) What is the specific gravity of concentrated commercial sulphuric acid ? How much sulphuric acid does it contain ? What is the present price per pound in carboy lots ?—*Worcester Polytechnic Inst, U S A*

11 Explain the reaction involved in the production of sulphuric acid in the "Chamber process" and the means adopted to prevent the escape of nitrous gases into the atmosphere Give two illustrations of the use of sulphuric acid as (*a*) a dehydrating agent, (*b*) an oxidizing agent —*Sheffield Univ*

12 In chemical literature at the present day reference is frequently made to "condensing agents" and substances are spoken of as "undergoing condensation" Explain these phrases, giving examples in illustration of your answer —*London Univ*

13 Chlorine is said to be an oxidizing agent, and sulphur dioxide a reducing agent, explain these statements and give examples illustrating these actions, stating any conditions which may be necessary Give also examples of reactions in which sulphur dioxide acts as a reducing agent —*London Univ*

14 What happens on heating with sulphuric acid (*a*) manganese dioxide (*b*) cuprous oxide, with nitric acid—(*a*) black oxide of iron, (*b*) red lead, with hydrochloric acid—(*a*) red oxide of iron, (*b*) black oxide of manganese —*London Univ*

15 The composition of a compound is barium 46 12 per cent, sulphur 21 54 per cent and oxygen 32 32 per cent What is the formula and name of the compound ?—*Glasgow Univ*

16 Explain the meaning of the term "nascent" in chemistry, illustrating your answer by reference to reactions in which (*a*) "nascent" hydrogen (*b*) "nascent" oxygen are supposed to take part —*Board of Educ*

CHAPTER XXIV

CHROMIUM, MOLYBDENUM, TUNGSTEN, AND URANIUM

§ 1 Potassium and Sodium Dichromates

Chromite —This mineral is also called chrome ironstone, or chrome iron ore It is a native ferrous chromite, $FeCr_2O_4$, or $Fe(CrO_2)_2$, contaminated with silica, alumina, magnesia, etc It resembles magnetite in general appearance, for it has an iron black colour, with a brownish tinge Good marketable chromite contains the equivalent of at least 50 per cent Cr_2O_3 and not more than about 10 per cent of silica. Most of the chromium compounds of commerce are derived from this ore

Manufacture of sodium chromate —The finely ground chromite is intimately mixed with lime and sodium carbonate, and roasted in an oxidizing atmosphere The reaction which occurs is probably $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 = 8Na_2CrO_4 + 8CO_2 + 2Fe_2O_3$ Possibly the ferrous chromite produces sodium chromite, $NaCrO_2$ thus $Fe(CrO_2)_2 + Na_2CO_3 = 2NaCrO_2 + FeO + CO_2$ The ferrous oxide and the sodium chromite are then oxidized by the air The object of the lime is to prevent fusion, and keep the mass porous to facilitate oxidation The roasted mass is then mixed with twice its weight of water, and an excess of soda ash is added to convert the calcium chromate formed during the reaction into sodium chromate The mixture is agitated for a couple of hours, and the solution of sodium chromate is separated from the insoluble matters by filter presses

Transformation of sodium chromate to the dichromate —The clear solution is then treated with sulphuric acid to neutralize the excess of alkali, and to convert the sodium chromate Na_2CrO_4, into sodium dichromate, $Na_2Cr_2O_7$, thus $H_2SO_4 + 2Na_2CrO_4 = H_2O + Na_2SO_4 + Na_2Cr_2O_7$ The clear solution is decanted from the precipitated sodium sulphate, and the solution is separated from the crystals by centrifugal separators. The solution is concentrated in iron pans, and when it has attained the specific gravity 1 7, it is filtered from the sodium sulphate which has separated during the evaporation Crystals of sodium dichromate separate on standing The yield is about 90 per cent of the theoretical

Conversion of sodium dichromate into the potassium salt —The sodium dichromate is converted into the potassium salt by mixing concentrated solutions of sodium dichromate with potassium chloride $Na_2Cr_2O_7 + 2KCl \rightleftharpoons K_2Cr_2O_7 + 2NaCl$ The potassium dichromate is at once precipitated The chromium is recovered from the mother liquid This apparently roundabout method of making sodium dichromate in

order to get the potassium salt is really cheaper than if potassium carbonate had been used in place of sodium carbonate, mainly because of the difference in cost between potassium carbonate, and between sodium carbonate and potassium chloride

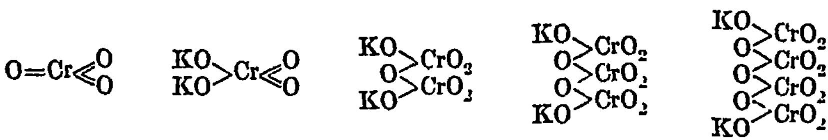
Properties of sodium and potassium dichromates—Potassium dichromate forms bright red triclinic crystals of the anhydrous salt, $K_2Cr_2O_7$, which melt at 400° The salt is easily purified by recrystallization because it is very much more soluble in hot than in cold water 100 grams of water dissolve 5 grams of the salt at 0°, 55 5 grams at 50°, and 129 grams at 100° The aqueous solution has an acid reaction The fact that potassium dichromate is so easily purified makes it a good starting point for the manufacture of chromium compounds generally Sodium dichromate crystals have the composition $Na_2Cr_2O_7 \cdot 2H_2O$ This salt is cheaper and more soluble in water than the potassium salt at ordinary temperatures At 0°, 100 grams of the solution contain 62 grams of $Na_2Cr_2O_7$, and at 80°, 80 grams of the salt.

§ 2 Chromic Acid and the Polychromates

Chromium trioxide, CrO_3—When a concentrated aqueous solution of potassium dichromate is treated with concentrated sulphuric acid, long scarlet needle like crystals separate when the solution is cooled The crystals can be filtered through glass wool and drained on a porous earthenware tile, then washed with concentrated nitric acid to remove the sulphuric acid, and sulphates, and dried in a current of dry warm air The resulting crystals of chromium trioxide, CrO_3, are very deliquescent, and dissolve in water, forming a red solution which is probably dichromic acid, $H_2Cr_2O_7$, formed by the reaction $2CrO_3 + H_2O = H_2Cr_2O_7$ The acid H_2CrO_4 has not been isolated Chromic trioxide, CrO_3, is thus called chromic anhydride, and the aqueous solution chromic acid, although the trioxide crystallizes out again when the aqueous solution is evaporated Chromium trioxide decomposes when heated to about 250° into chromic oxide Cr_2O_3, and oxygen $4CrO_3 = 2Cr_2O_3 + 3O_2$ Chromium trioxide is a vigorous oxidizing agent owing to the readiness with which it seems to part with oxygen to form chromic oxide, Cr_2O_3 Thus, alcohol dropped on to the oxide takes fire, ammonia is decomposed, paper is charred at once, carbonaceous matter is oxidized to carbon dioxide, etc

Potassium chromate, K_2CrO_4—If potassium hydroxide be added to an aqueous solution of potassium dichromate in the proportions indicated by the equation $K_2Cr_2O_7 + 2KOH = H_2O + 2K_2CrO_4$, a yellow solution of potassium chromate is obtained which furnishes bright yellow rhombic crystals when concentrated. The yellow crystals of potassium chromate, K_2CrO_4, are isomorphous with potassium sulphate Hence potassium chromate may be regarded as a salt formed by the union of one molecule of potash, K_2O, with one molecule of chromic anhydride, CrO_3, thus, $K_2O \cdot CrO_3$ or K_2CrO_4 The isomorphism with potassium sulphate suggests a similar structural formula with an atom of sexivalent chromium in place of sexivalent sulphur If normal chromates be treated with acids dichromates are formed $2K_2CrO_4 + 4HCl = 4KCl + H_2Cr_2O_7 + H_2O$ Potassium dichromate is a salt formed by the union of two molecules of the anhydride, CrO_3, with one molecule of the base $K_2O \cdot 2CrO_3$

Polychromates.—The radicle CrO_4'' is bivalent in the chromates, and the radicle Cr_2O_7'' is bivalent in the dichromates. By treating potassium dichromate with chromic oxide, or with boiling moderately concentrated nitric acid, potassium trichromate is formed: $K_2Cr_3O_{10}$, or $K_2O.3CrO_3$; and by treating the trichromate with concentrated nitric acid, potassium tetrachromate, $K_2O.4CrO_3$, or $K_2Cr_4O_{13}$, is formed. Just as in the formation of disulphuric or pyrosulphuric acid (*q.v.*) and its salts by the condensation of two molecules of H_2SO_4, so here, dichromic acid is considered to be a condensation product of two molecules of chromic acid, H_2CrO_4; and the dichromates—*e.g.* $K_2Cr_2O_7$, are analogous with the pyrosulphates, *e.g.* $K_2S_2O_7$. The constitutional formulæ of the chromates and dichromates are supposed to be analogous with the constitutional formulæ of the sulphates and pyro- or disulphates respectively:



Chromic trioxide, CrO_3	Potassium chromate, $K_2O.CrO_3$	Potassium dichromate $K_2O.2CrO_3$	Potassium trichromate, $K_2O.3CrO_3$	Potassium tetrachromate, $K_2O.4CrO_3$

The addition of an excess of alkali to the polychromates reconverts them into normal chromates. The phenomenon of condensation also occurs with many oxyacids—boric, iodic, and phosphoric acids—and particularly with molybdic and tungstic acids; it is slight with uranic acid, and unknown with nitric acid.

Chromates and dichromates.—When ammonium dichromate, $(NH_4)_2Cr_2O_7$, is heated, free nitrogen, water, and chromic oxide are obtained: $(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + 4H_2O + N_2$. Lead chromate, $PbCrO_4$, is a bright sulphur yellow salt precipitated by adding potassium chromate to the solution of a lead salt. It is used as a pigment under the name "chrome yellow." By boiling lead chromate with aqueous ammonia or potassium hydroxide, a basic lead chromate, $Pb(OH)_2.PbCrO_4$, called "chrome red," or "Austrian cinnabar," is formed. This also is used as a pigment. Barium chromate, $BaCrO_4$, is formed in a similar manner, and is used as a pigment. The precipitation of barium chromate from a solution of a barium salt by adding a soluble chromate; or conversely, the precipitation of chromium as barium chromate by adding a soluble barium salt, enables the amount of barium or of chromium in a solution to be determined. At 18° a litre of water only dissolves 0.0038 gram of barium chromate; 1.2 gram of strontium chromate; and 23.2 grams of calcium chromate. Calcium chromate, $CaCrO_4.2H_2O$, is isomorphous with calcium sulphate, $CaSO_4.2H_2O$. Silver chromate and mercurous chromate are both red salts. The chromates are often made by the addition of soluble dichromates to a solution of the salt in question. The ionic hypothesis describes the reaction thus: The dichromate ions, Cr_2O_7'', in the solution are partly broken down into CrO_4'' ions. For equilibrium: $Cr_2O_7'' + H_2O \rightleftharpoons 2CrO_4'' + 2H^{\cdot}$. If any $Pb^{\cdot\cdot}$ ions are present, the CrO_4'' ions are removed because $PbCrO_4$ separates from the solution. The supply of CrO_4'' ions is kept up by the continued dissociation of the Cr_2O_7'' ions until all the dichromate has been converted into chromate.

Potassium dichromate as an oxidizing agent.—Potassium dichromate is used in volumetric analysis in virtue of its oxidizing properties when in contact with a reducing agent, *e.g.* ferrous sulphate, $FeSO_4$. Since potassium dichromate has a formula equivalent to $K_2O.2CrO_3$, and ferrous sulphate a formula equivalent to $FeO.SO_3$, the $2CrO_3$ of the former on reduction furnish $2CrO_3 = Cr_2O_3 + 3O$; and the ferrous oxide FeO, of the latter is converted into Fe_2O_3, it follows that one molecule of potassium dichromate is equivalent in oxidizing properties to three atoms of oxygen and it can therefore oxidize six molecules of ferrous sulphate. Hence the equation can be written: $6FeSO_4 + K_2Cr_2O_7 = 3Fe_2O_3 + Cr_2O_3 + 6SO_3 + K_2O$. The action takes place in an acidified solution so that the ferrous sulphate is oxidized to ferric sulphate, $Fe_2(SO_4)_3$, the potassium oxide forms potassium sulphate, K_2SO_4, and the chromic oxide, chromic sulphate, $Cr_2(SO_4)_3$. In all, thirteen SO_4 radicles are needed, but six SO_4 radicles already come from the ferrous sulphate, hence seven molecules of sulphuric acid are needed. The full equation thus becomes: $6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$. Similarly, one molecule of potassium dichromate can oxidize three molecules of sulphurous acid, H_2SO_3, to sulphuric acid, H_2SO_4, and the equation is accordingly written: $K_2Cr_2O_7 + 3H_2SO_3 + H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O$. When heated with hydrochloric acid, chlorine is produced as indicated in our study of the action of oxidizing agents on hydrochloric acid.

Chromyl chloride, CrO_2Cl_2.—When potassium dichromate, a soluble chloride, and sulphuric acid are heated in a retort, a dark reddish-brown liquid, which boils at 116°, distils over. It is chromic oxychloride, or chromyl chloride CrO_2Cl_2. Chromyl chloride is decomposed into chromic acid and hydrochloric acid by contact with water: $CrO_2Cl_2 + 2H_2O = 2HCl + H_2CrO_4$. These reactions are used as a test for chlorides. Neither the bromide nor the iodide form corresponding compounds, so that if a mixture of these three halogens be distilled with sulphuric acid and potassium dichromate, the distillate, when treated with water, gives a solution which responds to the tests for chromic acid, the presence of chlorides may be inferred. Chromyl chloride is also formed by dissolving chromic trioxide in concentrated sulphuric acid, adding hydrochloric acid, drop by drop, and distilling the mixture as before: $CrO_3 + 2HCl = CrO_2Cl_2 + H_2O$. The sulphuric acid retains the water formed during the reaction. Yellowish-red crystals of potassium chlorochromate, $CrO_2Cl(OK)$, corresponding with the unknown chlorochromic acid, $CrO_2Cl(OH)$, are formed when a solution of potassium dichromate in hydrochloric acid is allowed to crystallize: $K_2Cr_2O_7 + 2HCl = H_2O + 2CrO_2(OK)Cl$. The two chlorides are supposed to be related to one another as follows:

$\genfrac{}{}{0pt}{}{O}{O}\!\geqslant Cr{=}O$	$\genfrac{}{}{0pt}{}{O}{O}\!\geqslant Cr \lessgtr \genfrac{}{}{0pt}{}{OH}{OH}$	$\genfrac{}{}{0pt}{}{O}{O}\!\geqslant Cr \lessgtr \genfrac{}{}{0pt}{}{OH}{Cl}$	$\genfrac{}{}{0pt}{}{O}{O}\!\geqslant Cr \lessgtr \genfrac{}{}{0pt}{}{Cl}{Cl}$
Chromic trioxide, CrO_3	Chromic acid, H_2CrO_4	Chlorochromic acid, $CrO_2Cl(OH)$	Chromyl chloride, CrO_2Cl_2.

Chromyl chloride thus appears to be analogous with sulphuryl chloride, SO_2Cl_2 (*q.v.*). Chromyl fluoride, CrO_2F_2, is known, but not the corresponding bromide and iodide. The chloride corresponding with chromium trioxide, namely, $CrCl_6$, has not been prepared.

Perchromic acid —A deep blue solution is obtained by treating dilute solutions of chromic acid, or acidified chromates with hydrogen peroxide This reaction is in common use as a means of detecting both chromic acid and hydrogen peroxide (*q v*) By shaking the mixture up with ether, an ethereal solution of the blue compound formed during the reaction can be obtained. By treating the blue solution with potassium at a temperature below —20°, hydrogen is copiously evolved, and a dark purple precipitate with the empirical composition $KCrO_4$ separates This decomposes at ordinary temperatures into potassium dichromate and oxygen $2K_2Cr_2O_8 = O_2 + 2K_2Cr_2O_7$ The blue solution must contain perchromic acid corresponding to this salt Lithium, sodium, magnesium, calcium, barium, and zinc perchromates have been prepared by the action of the acetates of these elements upon the blue solution Ammonia gas, at —40°, yields the ammonium salt If an excess of hydrogen peroxide be employed in the preparation of the blue solution, stable higher chromates have been produced Thus by adding a 30 per cent solution of hydrogen peroxide to an alcoholic solution of potassium perchromate, a dark red precipitate of another potassium perchromate, K_3CrO_8, is obtained This appears to be stable below 70°, and is considered to be a salt of an unknown acid, H_3CrO_8 We are, however, not very clear about even the empirical composition of these higher chromates, the methods of preparing pure salts are not satisfactory

§ 3 The Colours of Salt Solutions

According to the ionic hypothesis, the colour of a dilute aqueous solution of an electrolyte is an additive effect of the colours of the anions, the cations, and of the unionized molecule The colour of the latter may be quite different from the colours of the two former so that the colour changes as the solution is more and more diluted, until ionization is complete The action of water on cupric chloride or cupric bromide illustrates the idea very well Solid cupric chloride, $CuCl_2$, is a dark brown powder which, when treated with a very small quantity of water, gives a yellow solution This is supposed to represent the colour of the molecules $CuCl_2$ When the solution is still further diluted the colour becomes green, and finally blue The blue colour is supposed to represent the colour of the Cu ions, the Cl′ ions are supposed to be colourless. The green colour is due to the partial ionization of the salt, and the sensation of green is due to the mixing of the yellow colour of the $CuCl_2$ molecules with the blue colour of the Cu ions—

$$\underbrace{\underset{\text{Yellow}}{CuCl_2} \rightleftharpoons \underset{\text{Blue}}{Cu}}_{\text{Green}} + \underset{\text{Colourless}}{2Cl'}$$

If a concentrated solution of ammonium chloride or of hydrochloric acid be added to the blue solution, not too dilute, the ionization is supposed to be driven back, and blue cupric ions suppressed, as indicated on p 321, because the solution becomes green Feebly ionized chlorides, *e g* mercuric chloride, do not restore the green colour Other copper salts give similar results Dilute solutions of equivalent concentration give a similar colour in spite of the fact that the salts are different Hence it is

assumed that the Cu ions are coloured blue, and that the ions behave with respect to colour independently of one another

Since cobaltous chloride gives a pink colour in dilute solutions, it is inferred that Co ions are thus colour If concentrated hydrochloric acid be added, the solution becomes blue owing to the formation of blue cobaltous chloride molecules The same effect is produced by raising the temperature, the pink colour becomes blue because, it is said, the degree of ionization is decreased by raising the temperature The true explanation in the case of cobaltous chloride is probably not so simple as this, because while calcium chloride, $CaCl_2$, turns the red solution blue, zinc chloride, $ZnCl_2$, turns the blue solution red This is supposed to be due to the formation of complex salts, $CaCoCl_4$, which gives blue $CoCl_4''$ ions, and $Co(ZnCl_4)$ which yields colourless $ZnCl_4''$ ions and red Co ions Many other hypotheses have been suggested—hydration and dehydration isomerism, etc

Among the coloured ions Cu' is blue, Fe , Ni , Cr , MnO_4'' are green, Co red, Mn pale pink, MnO_4' purple, CrO_4'' yellow, Cr_2O_7'' orange red, etc The colourless ions include Cl', I', Br', CyS', NO_3', PO_4''', ClO_3', K , Na , Ca , Mg , Fe , Pb , SO_4'', etc The colours of the ions are deduced, as indicated above, from the effects of dilution on the colour of the aqueous solutions

The ionic hypothesis assumes that the difference in the colour of aqueous solutions of potassium chromate and potassium dichromate is due to the difference in the colours of the CrO_4'' ions of the chromates, and the Cr_2O_7'' ions of the dichromates, the former are yellow, the latter orange or red. The CrO_4'' ions are supposed to be unstable in the presence of the H ions of acids $2CrO_4'' + 2H = Cr_2O_7 + H_2O$, and the dichromate ions unstable in the presence of OH ions of alkaline solutions $Cr_2O_7'' + 2OH' = 2CrO_4'' + H_2O$ Since chromium trioxide, CrO_3, gives an orange coloured solution with water, it is inferred that dichromic, not chromic acid is formed when CrO_3 is dissolved in water This view is confirmed by observations on the depression of the freezing point of aqueous solutions of chromium trioxide and from measurements on the electrical conductivity of the aqueous solutions.

§ 4 Chromium Oxides and Hydroxides

Chromium hydroxide, $Cr(OH)_2$ By adding potassium hydroxide to a solution of chromous chloride (*q v*) a yellowish brown precipitate of chromous hydroxide is obtained which rapidly oxidizes in air. The corresponding chromous oxide, CrO, has not been obtained

Chromium sesquioxide, Cr_2O_3 This oxide is prepared as a dark green powder when ammonium dichromate is heated, or when a mixture of potassium dichromate and ammonium chloride is heated In the latter case, the potassium chloride is removed by washing the residue with water The oxide calcined at a high temperature is dissolved by acids very slowly

Chromic hydroxide, $Cr(OH)_3$, separates as a bluish gelatinous (colloidal) precipitate when ammonia is added to a solution of a chromic salt Chromic hydroxide dissolves in a solution of chromic chloride, and if the solution be dialyzed, as in the case of ferric chloride, a colloidal solution, hydrosol of chromic hydroxide, is obtained When freshly precipitated, chromic hydroxide readily dissolves in acids, but it is less rapidly dissolved if it

has stood some time When heated in air, it forms green chromic oxide, Cr_2O_3 Several important green pigments are made by preparing the oxide under special conditions, e g calcining potassium dichromate intimately mixed with sulphur, ammonium chloride, starch, boric acid, etc, and extracting the matters soluble in water Guignet's green, for instance, is made by calcining potassium dichromate with boric acid, etc Chromic sesquioxide, in an extremely fine state of subdivision, appears to be crimson, for if an intimate mixture of stannic oxide, or zinc oxide, or alumina, with a very small proportion of chromic oxide be heated to a high temperature in an oxidizing atmosphere a red powder is obtained There is some evidence to show that the red colour is not due to the formation of a chemical compound, and that the "chrome tin" colour is related to purple of Cassius (q v) The "chrome tin" crimson is used for colouring pottery, glazes, etc The chrome alumina colour can be prepared to appear green in daylight or in reflected light, and crimson in transmitted or in artificial light, thus resembling the mineral *alexandrite*. Chromium is the colouring agent of artificial rubies, first synthesized in 1837 by A Gaudin by melting together potassium dichromate and alumina in the oxyhydrogen blowpipe

Chromic hydroxide is a base, and forms salts—chromic chloride, sulphate, etc —when treated with the proper acid It is also a feeble acid, for, when freshly precipitated, it dissolves in alkali hydroxides presumably owing to the formation of alkaline chromites—e g $Cr(OH)_2OK$, or CrO OK, that is, $KCrO_2$ Native chromite is a ferrous chromite, $Fe(CrO_2)_2$, its constitution is probably analogous with the spinels (q v) The chromites are regarded as derivatives of an unknown chromous acid, $HCrO_2$ The soluble chromites are hydrolyzed when their aqueous solutions are boiled, and greenish chromic hydroxide is precipitated

§ 5 Chromium

History —In 1762 J G Lehmann, in a letter to the naturalist G L L de Buffon, described a new mineral from Siberia We now know this mineral to be crocoisite, or lead chromate Both L. N Vauquelin and Macquart, in 1789, failed to recognize in the mineral a new element, and both reported lead, iron, alumina, and a large amount of oxygen However, in 1797, L. N Vauquelin re examined the mineral and concluded that the lead must be combined with a peculiar acid which he considered to be the oxide of a new metal This he called chromium—from the Greek χρῶμα (chroma), colour—because its compounds are all coloured In 1798, L. N Vauquelin detected the new element in spinel and in smaragdite, and F Tassært found chromium in chrome iron ore in 1799

Occurrence —Metallic chromium does not occur free in nature It occurs combined with oxygen in *chrome ochre*, which is chromium sesquioxide, Cr_2O_3, associated with more or less earthy matters Chromite, $Fe(CrO_2)_2$, is the chief ore of chromium It also occurs as lead chromate in crocoite or *crocoisite*, $PbCrO_4$ Traces occur in many minerals—emerald, jade, serpentine, etc

Preparation of the metal —Chromium metal can be prepared by reducing chromium sesquioxide with carbon in the electric furnace, or better, by the aluminothermic process, which is also called, after its inventor, the H Goldschmidt's process (1905) An intimate mixture of chromium sesquioxide and aluminium powder, *A*, Fig 170, is placed in a

refractory clay crucible so that about two-thirds of the crucible is filled. A mixture of sodium or barium peroxide and aluminium powder is placed over this, as at *B*, Fig. 170. A piece of magnesium ribbon, *C*, is stuck into the latter mixture, and a layer of powdered fluorspar, *D*, is placed over all. The crucible is then set in a tray of sand and the magnesium ribbon, *C*, ignited. When the flame reaches the peroxide mixture, *B*, the aluminium is oxidized with explosive violence, and care must be taken to protect the face and hands accordingly. The heat of the combustion of the aluminium in the ignition mixture, *B*, starts the reaction between the chromic oxide and the aluminium. The chromic oxide is reduced to metal, and the aluminium is oxidized to alumina. $Cr_2O_3 + 2Al = 2Cr + Al_2O_3$. When the crucible is cold, a button of metallic chromium will be found on the bottom. The slag is nothing but fused alumina which has crystallized so as to form a kind of artificial corundum. This is called *corubin* to distinguish it from natural corundum. In Goldschmidt's works at Essen, about 100 kilograms of chromium are produced at a single charge. The reduction takes place in less than half an hour. Manganese is produced in a similar manner. Titanium, alloyed with iron—ferro titanium—is produced by the same process.

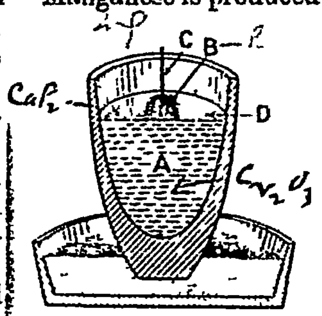


FIG. 170.—Alumino-Thermic Process for reduction of Oxides.

Properties of metallic chromium.—Chromium is a hard metal of a steel grey colour. A 98–99 per cent. sample melted at 1520°, and boiled about 2200°. The metal is fairly stable in air but oxidizes when heated to a high temperature, forming chromium sesquioxide, Cr_2O_3. The metal dissolves in dilute hydrochloric and sulphuric acids, forming respectively chromous chloride and chromous sulphate, with the evolution of hydrogen. When placed in contact with nitric acid, the metal becomes inert or passive, for it is then no longer attacked by acids which dissolve it under normal conditions. The phenomenon of "passivity" is discussed in connection with iron.

Atomic weight.—The combining weight of chromium has been determined from the amount of chromium in silver and barium chromates; in chromium sulphate; in ammonium chromium alum; chromium chloride, potassium and ammonium dichromates, etc. The results show that if oxygen be 16, the combining weight of chromium lies somewhere between 51.6 and 53.5. The atomic weight is generally taken to be 52.1, O = 16. This number agrees with Dulong and Petit's rule, for the specific heat of chromium is 0.12, and 6.4 ÷ 0.12 furnishes the number 53.3. This number is sufficiently close to 52.1 to show that 52.1 represents the atomic weight of chromium if Dulong and Petit's rule applies to chromium.

Uses.—Ferro-chromium alloys are made containing over 60 per cent. of chromium and less than 2 per cent. of carbon by smelting high-grade chromites in the electric furnace. Ferro-chromium is used in the manufacture of chrome-steel. Chrome-steel is a hard, tough, and dense metal with a high tensile strength. Steel with 1 to 1½ per cent. of carbon and 2½ to 4 per cent. of chromium is so hard that it cannot be worked by ordinary hardened tool steels—for example, it is drill proof. It can, however,

be welded to iron, and rolled into sheets, etc It is used in the manufacture of burglar proof safes, cutlery, stamp mill shoes, crusher jaws, *knuckles for car couplings, etc It is superior to every known metal* for the wearing parts of crushing and pulverizing mills. Alloys of chromium, nickel, and iron are used for the armour plates of war-ships The alloy is hard and elastic, and even if a projectile does penetrate the armour plating the metal does not crack.

Chromite is used in making the hearths of steel furnaces since it can be used as a neutral refractory material between the basic (magnesian) bricks in the interior of the furnace, and the acidic (siliceous) bricks outside. Chromite bricks are not injured by contact with basic, nor with acid bricks, whereas acidic and basic bricks, when heated in contact with one another, are likely to fuse at the surfaces of contact owing to the formation of fusible silicates. The bricks are very refractory—softening between 2000° and 2100°—and do not crack by sudden heating and cooling

Potassium and sodium chromates are used in dyeing, in the manufacture of pigments (chrome yellow, chrome red, Guignet's green, etc), in tanning leather, etc Chromic trioxide is used in place of nitric acid in some voltaic batteries, etc

§ 6 Molybdenum, Tungsten, and Uranium

	Molybdenum, Mo	Tungsten, W	Uranium, U
Atomic weight	96	184	238 5

Molybdenum Mo.

The term μόλυβδος (molybdos) was applied by the Greeks to galena and other lead ores Up to the middle of the eighteenth century, the mineral molybdite or molybdenite was supposed to be identical with graphite, then known as "plumbago" or "black lead" In 1778, K. W Scheele, in his *Treatise on Molybdena*, showed that, unlike plumbago or graphite, molybdenite forms a "peculiar white earth" when treated with nitric acid This he proved to have acid properties, and he called it "acidum molybdenæ," that is, molybdic acid, and he correctly considered the mineral molybdenite to be a molybdenum sulphide In 1790, P J Hjelm isolated the element as a metallic powder by heating molybdic acid with charcoal

Molybdic trioxide, MoO_3, is the most important compound of molybdenum Like the analogous chromic trioxide, it behaves as an acid anhydride, forming molybdic acid, H_2MoO_4, and salts are called molybdates A solution of ammonium molybdate dissolved in an excess of nitric acid is used as a test for phosphates because it gives a yellow precipitate of ammonium phosphomolybdate with solutions containing phosphates A similar precipitate is produced with arsenates The composition of the precipitate varies a little with the conditions under which it is formed, so that the amount of As_2O_5 or P_2O_5 associated with a given amount of the precipitate is not always the same, consequently, in quantitative work, the precipitate is usually redissolved and the phosphorus re precipitated as magnesium ammonium phosphate (*q v*) which is more easily controlled.

The variable composition of precipitated ammonium phosphomolybdate *may seem to violate the "constancy of composition" test for distinguishing*

compounds from mixtures It has been stated that "there are no exceptions to the law of constant composition," the real meaning of the phrase is that a compound is defined as a substance of constant composition, and we refuse to call any other substance a chemical compound As P Duhem (1902) has pointed out, so long as we do this there can be no exceptions to the law In the present case, the difficulty is usually referred to the tendency of chromic, molybdic, and tungstic acids to condense and form complex salts of the type $R'_2O\,nCrO_3$, $R'_2O\,nMoO_3$, and $R'_2O\,nWO_3$, where n represents the numerical ratio between the CrO_3, etc, and the R'_2O groups Salts of acids more hydrated than H_2MoO_4 are known Ordinary ammonium molybdate, for instance, is $(NH_4)_6Mo_7O_{24}\,4H_2O$, ordinary sodium tungstate is $Na_{10}W_{12}O_{41}\,28H_2O$, that is, $5Na_2O\,12WO_3.28H_2O$ In addition to this, molybdic and tungstic acids can unite with one or more molecules of phosphoric, arsenic, silicic and other acids, forming still more complex acids, thus, we have phospho-, arseno-, arseni-, vanadi-, and silici- molybdic and tungstic acids, etc Chromium, as we have seen, forms a similar series of acids, uranium exhibits but a slight tendency to form complex acids

The more important oxides of molybdenum are MoO, Mo_2O_3, MoO_2, MoO_3, and in addition, several complex oxides appear to exist—Mo_2O_5 or $MoO_2\,MoO_3$, Mo_3O_8 or $MoO_2\,2MoO_3$, Mo_5O_{12} or $3MoO_2\,2MoO_3$ The molybdates are reduced by zinc in acid solution to one of the lower oxides approximately, Mo_2O_3, and at the same time the colour of the solution changes through various shades of violet, blue, and black A reddish-brown molybdenum sulphide is precipitated by hydrogen sulphide in acid solution The chlorides of molybdenum $MoCl_2$, $MoCl_3$, $MoCl_4$, $MoCl_5$ and $MoCl_6$ are known Hence molybdenum is 2-, 3-, 4, 5-, and 6-valent

Molybdenum steel is hard and less brittle than tungsten steel Molybdenum is said to be far more effective than tungsten in the manufacture of hard steels. Molybdenum steel is used for making rifle barrels, propeller shafts, etc, and particularly high speed tool steels These steels, unlike ordinary carbon steels, have the peculiar property of retaining their "temper" when heated to a high degree, so that it is possible to make heavy cuts at high speed, for the steel can be heated to dull redness without impairing its quality Molybdenum steel contains up to 10 per cent of molybdenum Molybdenum is also used as a blue pigment in porcelain painting, in silk and woollen dyeing, and in colouring leather and rubber Ammonium molybdate is largely used in the determination of phosphorus in iron and steel laboratories

Tungsten, W

Up to the middle of the eighteenth century, the mineral scheelite—formerly called "tungsten" (heavy stone)—and wolframite were supposed to be ores of tin, but, in 1781, K. W Scheele demonstrated that scheelite contains a peculiar acid, which he called tungstic acid, united with lime as a base The same year, T Bergmann recognized tungstic acid as an oxide of a new element, tungsten, which was isolated by J J y Don Fausto d'Elhuyar in 1783 The tungsten compounds are somewhat similar to those of molybdenum The chlorides—WCl_2, WCl_4, WCl_5, and WCl_6—show that tungsten may be 2-, 4-, 5-, and 6 valent Fabrics which have been

soaked in a solution of sodium tungstate and then dried do not burn with a flame but smoulder away slowly, hence sodium tungstate is used in making articles of clothing—*e g* flannelette—which the makers style "non-inflammable"—an insoluble tungstate is precipitated in the fibres of the fabric Sodium tungstate is used as a mordant in dyeing Lead tungstate has been used as a substitute for white lead in painting The trioxide is used as a canary yellow pigment Tungsten is also used in making high speed steels—see "Molybdenum"

Uranium, U

The mineral pitchblende was formerly supposed to be an ore of zinc, iron, or tungsten, but M. H. Klaproth (1789) proved that it contained what he styled a "half metallic substance" different from the three elements just named This element was named "uranium," in honour of Herschel's discovery of the planet Uranus in 1781 E M. Péligot proved that Klaproth's element was really an oxide of uranium, and he isolated the metal itself in 1842

Uranium forms five oxides—U_2O_3, UO_2, U_3O_8, UO_3, UO_4 The chlorides UCl_3, UCl_4, UCl_5, UO_2Cl_2, and a fluoride UF_6 are known Hence uranium is 3, 4-, 5, and 6 valent Uranium is quadrivalent in the uranous salts, and sexivalent in the uranic salts, The uranic salts are derived from uranic acid, $UO_2(OH)_2$ Thus, uranic nitrate is $UO_2(NO_3)_2.6H_2O$, uranic chloride is UO_2Cl_2, etc The group UO_2 is generally called uranyl, and the salts just named are respectively uranyl nitrate and uranyl chloride, Uranic trioxide, UO_3, has also acidic properties, for it forms salts mono, di, tri, and tetra uranates, analogous in constitution with the corresponding chromates (p 466) Thus sodium diuranate is $Na_2U_2O_7.6H_2O$, etc Sodium diuranate is called uranium yellow, and is used, as well as uranium oxide, for colouring glass and pottery glazes Uranium is also used in the manufacture of incandescent mantles When alloyed with steel, it makes the metal tough and hard Solutions of uranyl nitrate or uranyl acetate are used in the volumetric determination of phosphoric acid If a solution containing a known amount of, say, uranyl nitrate be added to a solution containing soluble phosphates, a greenish yellow precipitate of uranyl ammonium phosphate, $UO_2(NH_4)PO_4$, insoluble in acetic acid, will be formed as long as any phosphate remains in the solution, When the phosphates are all precipitated, any further addition of the standard solution of uranyl nitrate will cause the solution to give a brown coloration when a drop is brought in contact with a drop of a solution of potassium ferrocyanide on, say, a white plate

Molybdenum occurs as *molybdenite*, that is, molybdenum sulphide, MoS_2, *wulfenite*, lead molybdate, $PbMoO_4$, uranium occurs as *pitchblende*, or *uraninite*, U_3O_8, and tungsten as *wolfram*, $FeWO_4$, and *scheelite*, $CaWO_4$ The metals are made by reducing the oxides or salts with reducing agents—carbon, potassium cyanide, hydrogen, sodium, or aluminium

§ 7 The Relationship of the Chromium Family

The metals chromium, molybdenum, tungsten, and uranium are difficult to fuse, their physical properties are indicated in the following table —

TABLE XXXI —PHYSICAL PROPERTIES OF THE CHROMIUM FAMILY

	Chromium	Molybdenum	Tungsten	Uranium
Atomic weight	52 1	96	184	238 5
Specific gravity	6 74	9 01	19 13	18 7
Atomic volume	7 7	10 6	9 6	12 7
Melting point	1500°	c 2450°	3267°±30°	1500°

The metals combine directly with oxygen, sulphur, nitrogen, and the halogens when heated in an atmosphere of these gases The oxides are difficult to reduce The trioxides—CrO_3, MoO_3, WO_3, UO_3—are acidic, and they form salts of the type K_2RO_4 as indicated above The formation of complex acids is also noteworthy The relationship of the chromium family with the sulphur family is brought out by the analogy between potassium chromate and sulphate, sodium chromate and sulphate, sulphuryl and chromyl chlorides, dichromates, disulphates, and diuranates, etc Starting with the elements with the smallest atomic weight, the relationship between the chromium and sulphur families is generally shown by a scheme like that in the margin The fault with this scheme is that it makes the relationship appear closer than the known facts would lead us to suppose; and the student might reasonably think that there is a tendency to go a begging for analogies between unrelated elements Chromium also has some analogies with metals of other groups, *e g* aluminium and trivalent iron (*q v*)

Questions

1 The oxide of chromium, Cr_2O_3, and the hydroxide, $Cr(OH)_3$, are weak basic and still more weakly acidic How does this statement accord with the fact that the salt, $Cr_2(SO_4)_3$, is stable in water while the corresponding carbonate and sulphide are not stable? What compound is formed when sodium carbonate is added to a solution of a chromic salt?—*Massachusetts Inst Technology, U S A*

2 What reaction takes place when thermit is ignited? What uses are made of thermit? How is metallic aluminium prepared commercially?—*Cornell Univ, U S A*

3 Mention any conditions which you know to affect the colour of metallic salts in solution Discuss the colour phenomena of solutions of cupric, chromic and ferric salts —*St Andrews Univ*

4 What happens when sodium hydroxide is mixed with a solution of a chromic salt? Of a potassium chromate solution? Of a potassium dichromate solution? Give four reactions which distinguish chromium from all other elements —*Amherst Coll, U S A*

5 Describe how you would prepare (*a*) barium chloride crystals from heavy spar, (*b*) potassium dichromate from chromium sesquioxide, (*c*) sodium carbonate and sodium bicarbonate from caustic soda?—*Aberystwyth Univ*

6 Nilson and Petterson found that 0 0859 gram of chromium sesquichloride when volatilized at 1200° C displaced 12 049 c c of gas (reduced to 0° C and 760 mm) calculate the density of the vapour compared with air and the formula to which it corresponds How would you prepare potassium chromate, potassium bichromate, and chromic acid?—*Owens Coll*

7 On heating an unknown quantity of potassium dichromate with a concentrated solution of hydrogen chloride, and passing the evolved gas into a solution of potassium iodide, 1 25 grams of iodine were liberated what was the weight of the dichromate used? (K = 39, I = 127, Cr = 52)

8 What use has been made of aluminium for the isolation of other metals? The heat of combustion of aluminium per gram is 7250, of sodium 2170, and of carbon 8000 calories From these data determine whether it is possible to reduce aluminium or sodium from their oxides by carbon —*Board of Educ*

CHAPTER XXV

MANGANESE

§ 1 Manganese Oxides

Manganese dioxide, MnO_2—The mineral *pyrolusite*, commonly contains from 70 to 90 per cent. of manganese dioxide, MnO_2, contaminated with more or less iron, alumina, silica, lime, baryta, and may be cobalt When heated, manganese dioxide loses oxygen and changes to manganese sesquioxide, Mn_2O_3, and then to mangano manganic oxide, Mn_3O_4 Cold concentrated hydrochloric acid gives a dark brown liquid, and very little chlorine is evolved The cold solution probably contains manganese trichloride, $MnCl_3$, and possibly also a little manganese tetrachloride, $MnCl_4$, but the composition of the liquid is not definitely known In any case, chlorine gas (*q v*) is evolved when the liquid is warmed, and manganous chloride, $MnCl_2$, remains in solution When heated with sulphuric acid, a solution of manganese sulphate, $MnSO_4$, is formed and oxygen gas is evolved $2MnO_2 + 2H_2SO_4 \rightarrow 2MnSO_4 + 2H_2O + O_2$.

Manganese dioxide appears to be a feeble acidic oxide, but since it dissolves in acids with the evolution of oxygen or its equivalent, it is probably an extremely feeble basic oxide, if at all There is no direct evidence of the existence of manganese tetrachloride, $MnCl_4$, in aqueous solution, but double salts, $MnCl_4 \, 2KCl$, or rather complex salts, K_2MnCl_6, are known, *cf* p 258 Manganese dioxide does not give hydrogen peroxide with acids, and it is not therefore a "superoxide" $Mn\genfrac{}{}{0pt}{}{<O}{<O}$, it is usually represented as a "polyoxide," $O{=}Mn{=}O$, although some consider it to be $(MnO_2)_2$—a manganous manganate $Mn{=}MnO_4$—as shown graphically on p 479 The constitution of manganese dioxide has not yet been made clear

Manganic sulphate, $Mn_2(SO_4)_3$ is obtained as a dark green powder when manganese dioxide is gently heated with concentrated sulphuric acid The manganic sulphate is immediately hydrolyzed by water, and it forms a series of "alums," isomorphous with aluminium alums, when treated with alkaline sulphates Thus, manganic potassium alum, $Mn_2(SO_4)_3 \, K_2SO_4 \, 24H_2O$, crystallizes in violet octahedral crystals The alums are rather more stable than manganic sulphate itself, but even then the potassium and ammonium manganic alums are so unstable that it is doubtful if they have been made pure, for they are hydrolyzed by water, forming manganic hydroxide, $Mn(OH)_3$. Cæsium and rubidium manganic alums are fairly stable

Hydrated manganese dioxide, $MnO_2.H_2O$, or manganous acid, H_2MnO_3.—When an alkaline hypochlorite or hypobromite (or an alkaline hydroxide with chlorine or bromine water) is added to an aqueous solution of a manganous salt, say, manganous chloride, $MnCl_2$, the so called "hydrated manganese oxide $MnO_2.H_2O$," is precipitated just as lead dioxide is precipitated from a lead salt solution under similar conditions. The reaction is represented: $2MnCl_2 + 4NaOCl = 2MnO_2 + 4NaCl + 2Cl_2$. The compound $MnO_2.H_2O$ is possibly a manganous acid, H_2MnO_3. A colloidal solution of this acid is easily obtained. Many compounds of manganese dioxide with the basic oxides are known. The "manganese mud" formed by blowing air through a solution containing a mixture of lime with a solution of manganese chloride is supposed to contain calcium manganite—$CaO.MnO_2$, or $CaMnO_3$. Calcium manganite is insoluble in water and slowly settles as a black mud—p. 234.

Manganese sesquioxide, Mn_2O_3.—Also called red oxide of manganese. It occurs in nature as *braunite*, Mn_2O_3, or rather $3Mn_2O_3.MnSiO_3$. Manganese sesquioxide is obtained as a black powder when any other oxide of manganese is heated to about 900° in a current of oxygen. The corresponding manganic hydroxide, $MnO.OH$, is formed when manganic sulphate is decomposed by water. This compound is converted into manganese dioxide when calcined to about 300°. The salts, manganic sulphate and manganic chloride have been described. With concentrated hydrochloric acid, the hydroxide seems to furnish manganese trichloride (*q.v.*). This shows that manganese sesquioxide possesses basic functions. Neither the oxide nor the hydroxide seems to dissolve in cold sulphuric acid; hot dilute sulphuric acid forms manganous sulphate, $MnSO_4$, and leaves manganese dioxide insoluble. With hot nitric acid, manganous nitrate and manganese dioxide are formed: $2MnO.OH + 2HNO_3 \rightarrow Mn(NO_3)_2 + MnO_2 + 2H_2O$. Hence, this oxide is sometimes represented as $MnO.MnO_2$ or better as manganous manganite, $Mn.MnO_3$, analogous with calcium manganite. The manganites are thus represented graphically:

$$\mathrm{O{=}Mn}{<}^{\mathrm{OH}}_{\mathrm{OH}} \qquad \mathrm{O{=}Mn}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Ca} \qquad \mathrm{O{=}Mn}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Mn}$$

Manganous acid. Calcium manganite. Manganous manganite.

This is hypothesis; however, trivalent manganese compounds are known, and manganese sesquioxide may be one of them: $O{=}Mn{-}O{-}Mn{=}O$.

Mangano-manganic oxide, Mn_3O_4.—This oxide occurs in nature in red prismatic crystals of *hausmannite*, and it is formed as a brownish-red powder when any of the manganese oxides are ignited in air. It can be obtained in a crystalline condition by heating the powdered oxide *in a current* of hydrogen chloride. Mangano-manganic oxide is not a simple basic oxide, for its behaviour towards acids leads to the *formation of a* soluble manganous salt, and insoluble manganese dioxide: $Mn_3O_4 + 2H_2SO_4 \rightarrow 2MnSO_4 + H_4MnO_4$. The hydrate then decomposes into manganese dioxide and water. Hence mangano-manganic oxide appears to be a compound oxide—$2MnO.MnO_2$, or $MnO.Mn_2O_3$, or better still, manganese orthomanganite, Mn_2MnO_4. The action of nitric acid indicated above may then be written: $Mn_2MnO_4 + 4HNO_3 \rightarrow 2Mn(NO_3)_2 + H_4MnO_4$. The oxide, Pb_3O_4 (*q.v.*), is generally supposed to have the constitution, Pb_2PbO_4, or $2PbO.PbO_2$, and Fe_3O_4, is supposed to be

$FeO.Fe_2O_3$, since no oxide corresponding with quadrivalent iron—FeO_2—is known to exist. Hence our theory of the constitution of Mn_3O_4 depends upon what view is taken of the constitution of Mn_2O_3. A red solution, containing manganous and manganic sulphates, is formed when Mn_3O_4 is treated with concentrated sulphuric acid, this corresponds with the formula $MnO.Mn_2O_3$ for mangano manganic oxide, and the formation of manganese dioxide and manganous salt when mangano manganic oxide is treated with dilute sulphuric or nitric acid agrees with Mn_2MnO_4, or $2MnO.MnO_2$, that is, with

$$Mn{<}^{O}_{O}{>}Mn{<}^{O}_{O}{>}Mn$$

Manganous oxide, MnO.—When manganous chloride is treated with an alkaline hydroxide, in the absence of air, a colourless flocculent precipitate of **manganous hydroxide**, $Mn(OH)_2$, is formed. This quickly oxidizes probably to green manganic hydroxide, $Mn(OH)_3$. The hydroxide is slightly soluble in water. If ammonium salts be present, a soluble complex salt, say, $(NH_4)_2MnCl_4$, is formed. Hence, the complete precipitation of manganese hydroxide by ammonia is prevented by the simultaneous formation of ammonium salts. If the ammoniacal solution of manganese hydroxide be exposed to air, **manganic hydroxide**, $Mn(OH)_3$, is slowly precipitated.

If sodium carbonate be added to a solution of a manganous salt, **manganous carbonate**, $MnCO_3$, is precipitated. If manganous carbonate or hydroxide be heated in the absence of air, or if any of the hydroxides of manganese be heated in a current of hydrogen gas, Mn_2O_3 is first formed; at 280° Mn_3O_4 is produced; and finally a greenish powder of manganous oxide, MnO, is obtained. This oxidizes rapidly on exposure to the air. The manganous salts are readily obtained by treating the carbonate or hydroxide with the proper acid. The manganous salts are pink in colour; the aqueous solutions are almost colourless. Unlike the ferrous salts, the manganous salts are stable in the solid condition, and also in neutral or acid solutions. Manganous chloride and sulphate both form double or complex salts with the alkali salts—$MnCl_2.2NH_4Cl.H_2O$; $MnSO_4.K_2SO_4.6H_2O$. Manganese and iron form similar isomorphous double salts, p. 258.

§ 2 Manganates and Permanganates.

Manganates.—When manganese dioxide is fused with potassium or sodium hydroxide, in the absence of air, a part of the manganese is converted into the corresponding manganate, *e.g.* $3MnO_2 + 2KOH = K_2MnO_4 + Mn_2O_3 + H_2O$. If air be present, and if some oxidizing agent—potassium nitrate or chlorate—be associated with the mixture, the manganese dioxide can be nearly all converted into potassium manganate: $2MnO_2 + 4KOH + O_2 = 2K_2MnO_4 + 2H_2O$. The fused mass has a dark green colour, and when diluted with a small quantity of water, it furnishes a dark green solution from which dark green crystals of potassium manganate, K_2MnO_4, can be obtained by allowing the solution to evaporate, at ordinary temperatures, in vacuo. Sodium manganate can be made by a similar process using sodium in place of potassium compounds; and it can also be made by fusing manganese dioxide and other manganese

compounds with sodium peroxide The sodium manganate, $Na_2MnO_4.10H_2O$, has a composition resembling Glauber's salt, $Na_2SO_4.10H_2O$ The isomorphism of sodium manganate with sodium sulphate and sodium chromate makes it probable that all these compounds have a similar constitution, and that like sulphur in the sulphates, manganese is sexivalent in the manganates By analogy with the sulphates, therefore, the graphic formula of potassium manganate is written

$\begin{matrix}O\\O\end{matrix}\!\!\geqslant Mn<\!\!\begin{matrix}OK\\OK\end{matrix}$	$\begin{matrix}O\\O\end{matrix}\!\!\geqslant Mn<\!\!\begin{matrix}O\\O\end{matrix}\!\!>Ba$	$\begin{matrix}O\\O\end{matrix}\!\!\geqslant Mn<\!\!\begin{matrix}O\\O\end{matrix}\!\!>Mn$
Potassium manganate	Barium manganate	Manganous manganate

Permanganates.—When the green concentrated solution of potassium manganate is gently warmed, or largely diluted with water, the green colour changes to pink owing to the formation of a solution of potassium permanganate, $KMnO_4$, and a precipitation of hydrated manganese dioxide, $MnO_2.H_2O$, thus $3K_2MnO_4 + 3H_2O = 2KMnO_4 + MnO_2.H_2O + 4KOH$ It is supposed that the potassium manganate is first hydrolyzed, forming manganic acid $K_2MnO_4 + 2H_2O = 2KOH + H_2MnO_4$, and that the manganic acid is so unstable that it is decomposed at once, $3H_2MnO_4 = 2HMnO_4 + MnO_2.H_2O + H_2O$ The manganate is thus self-oxidized and self-reduced for the manganate is decomposed into a compound richer in oxygen and at the same time into a compound poorer in oxygen One part of the compound is oxidized at the expense of the oxygen in another part Several examples of this phenomenon have already been given—the decomposition of hypochlorites into chlorates and chlorides, the ignition of a chlorate gives a perchlorate and a chloride, while alkaline thiosulphates and sulphites give, on calcination in the absence of air, sulphates and sulphides We shall also find later that nitrous acid furnishes nitric acid and nitric oxide, hypophosphorous and phosphorous acids give phosphoric acid and phosphine Potassium manganate is not hydrolyzed in alkaline solutions, and it is supposed that pure water will not hydrolyze the solution If a small trace of acid be present, even carbonic acid derived from the atmosphere, the hydrolysis takes place Hence if carbon dioxide be passed through an aqueous solution of potassium manganate, the latter is converted into a permanganate $K_2MnO_4 + H_2CO_3 = K_2CO_3 + H_2MnO_4$, and the manganic acid is then decomposed as indicated above This is one method of making potassium permanganate, or, solutions of potassium manganate can be oxidized by means of chlorine, ozone, hydrogen peroxide, and other oxidizing agents

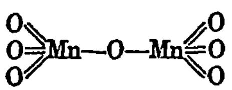
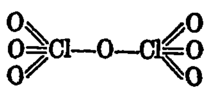
Potassium permanganate forms dark purple, almost black crystals with a greenish lustre The crystals are isomorphous with potassium perchlorate, $KClO_4$ The isomorphism makes it probable that manganese in potassium permanganate is septivalent, and that the compound has the graphic formula

$$\begin{matrix}O\\O\\O\end{matrix}\!\!\equiv Mn—OK$$

The crystals are moderately soluble in water 100 grams of water at 0° dissolve 2.83 grams of the salt, and at 50° 16.89 grams. The saturated solution is an intense purple colour

When heated to about 240°, potassium permanganate furnishes oxygen and potassium manganate $6KMnO_4 = 3K_2MnO_4 + 3MnO_2 + 3O_2$. With concentrated sulphuric acid, it decomposes explosively $4KMnO_4 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2$, but it is not decomposed by very dilute sulphuric acid, hot or cold. If a hot aqueous solution of silver nitrate and potassium permanganate be cooled, silver permanganate, $AgMnO_4$, separates, and if the solution of silver permanganate be treated with barium chloride, barium permanganate, $Ba(MnO_4)_2$, and insoluble silver chloride are formed.

Permanganic acid and its anhydride—Potassium permanganate is a salt of permanganic acid, $HMnO_4$ Permanganic acid is best made by adding just sufficient sulphuric acid to barium permanganate to convert all the barium into barium sulphate On evaporating the filtered solution, violet crystals of permanganic acid are obtained. Like perchloric acid, $HClO_4$, permanganic acid, $HMnO_4$, is a powerful oxidizing agent, and like perchloric acid, it decomposes in contact with organic matter If solid potassium permanganate be cautiously added to well cooled concentrated sulphuric acid, a green oily liquid is obtained which appears to be $(MnO_3)_2SO_4$ If a little water be added to this solution, well cooled, a dark reddish brown liquid separates which does not solidify at −20° This is supposed to be manganese heptoxide, Mn_2O_7 $(MnO_3)_2SO_4 + H_2O = Mn_2O_7 + H_2SO_4$, or graphically, by analogy with chlorine heptoxide

Manganese heptoxide is very unstable, and decomposes with violence when warmed, forming a lower oxide and oxygen $2Mn_2O_7 = 4MnO_2 + 3O_2$ A mixture of sulphur, or phosphorus with potassium permanganate, is violently explosive Manganese heptoxide is permanganic anhydride, because, when treated with cold water and sulphuric acid, it regenerates the green solution of $(MnO_3)_2SO_4$

Manganic acid and its anhydride—If solid potassium permanganate be dissolved in concentrated sulphuric acid, and the green solution—probably of $(MnO_3)_2SO_4$—be dropped upon dry sodium carbonate, violet fumes are evolved. These fumes may be condensed to a red viscid solid not yet proved to be MnO_3, manganic anhydride or manganese trioxide The permanganic anhydride is probably decomposed by the reaction $2Mn_2O_7 = 4MnO_3 + O_2$. Manganese trioxide is decomposed by water $3MnO_3 + H_2O = 2HMnO_4 + MnO_2$. Manganic acid, H_2MnO_4, might be expected to be a product of this reaction, but manganic acid has not been prepared in the pure state

Oxidizing action of the permanganates—Potassium permanganate is not acted upon by pure sodium or potassium hydroxides in aqueous solutions, but the commercial alkaline hydroxides generally contain sufficient impurities to reduce some of the permanganate When heated with an alkali, potassium permanganate reverts to potassium manganate $4KMnO_4 + 4KOH = 4K_2MnO_4 + 2H_2O + O_2$, if a reducing agent be present, the alkaline permanganate solution is further reduced to manganese dioxide $4KMnO_4 + 2H_2O = 4MnO_2 + 4KOH + 3O_2$, while in acidified solutions, the

reduction proceeds still further, and a manganous salt is formed: $4KMnO_4 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2$ There are thus three stages in the reduction of potassium permanganate corresponding with the separation of 1, 3, and 5 atoms of oxygen per two molecules of salt, the decomposition products are respectively potassium manganate, manganese dioxide, and a manganous salt In symbols

$$Mn_2O_7 \rightarrow 2MnO_3 + O, \quad Mn_2O_7 \rightarrow 2MnO_2 + 3O, \quad Mn_2O_7 \rightarrow 2MnO + 5O$$

The first takes place in alkaline solutions, the second in alkaline and reducing solutions, and the third in acid solutions

Oxalic acid, ferrous sulphate, sulphurous acid, hydrogen peroxide, nitrous acid, etc, reduce potassium permanganate to a manganous salt in an acid solution Since the solution of the manganous salt is almost colourless, if a solution of potassium permanganate containing a known amount of the salt per litre, be added from a burette, the permanganate is decolorized as fast as it is added to the reducing agent, until all the latter has been oxidized. The appearance of a permanent pink coloration due to the permanganate shows that all the reducing agent is destroyed The solution must be kept acid or a precipitate of hydrated manganese dioxide will be formed.

§ 3 Manganese

History—Manganese appears to have been used by the ancient Egyptians and Romans for bleaching glass Pliny mentions its use for this purpose under the name "magnes" B Valentine and many later chemists believed wad to be an ore of iron J H Pott (1740) proved that pyrolusite proper does not contain iron, and prepared a number of salts from it K. W Scheele (1774) made an important investigation on manganese (*vide* chlorine), and T Bergmann (1774) concluded from Scheele's experiments that pyrolusite contained a new metal which was afterwards isolated by J F John in 1807

Occurrence—The metal manganese does not occur free in nature The chief minerals are the oxides *pyrolusite*, MnO_2, *braunite*, Mn_2O_3, *hausmannite*, Mn_3O_4, *manganite*, $Mn_2O_3.H_2O$ The carbonate, $MnCO_3$, is often associated with siderite ($FeCO_3$), manganese also occurs as sulphide, *manganese blende*, MnS *Wad* is an impure mixture of manganese oxides often found in damp low-lying places Wad is supposed to be a decomposition product of the manganese minerals Minute quantities of manganese occur in water, plants, and animals, and traces also appear to be the colouring agent of many amethyst-coloured minerals

Preparation of the metal—Metallic manganese has been obtained by reducing the oxide with carbon when a very high temperature is required It is far better to mix dry manganese dioxide with dry aluminium powder in a crucible, and to ignite the mixture as in Goldschmidt's process, Fig 170, for the reduction of chromium oxide $3MnO_2 + 4Al = 2Al_2O_3 + 3Mn$ The metallic manganese and alumina are melted by the high temperature, and the metal collects at the bottom of the crucible

Properties of the metal—Manganese is a grey metal with a reddish tinge like bismuth The metal is brittle and harder than iron It has a density of 8·0, melts at 1245° and boils at 1900° The metal volatilizes in

the electric arc furnaces. Manganese is superficially oxidized when exposed to the air, and it decomposes in contact with water with the evolution of hydrogen. When heated in nitrogen, it forms manganese nitride, Mn_5N_2, and if heated in ammonia it forms another nitride, Mn_3N_2. It also combines directly with carbon to form manganese carbide, Mn_3C. It reacts with nitrogen at about 1200°. Manganese readily dissolves in acids—hydrochloric acid, nitric acid, and acetic acid—forming manganous salts with the evolution of hydrogen gas. The valency of manganese is noteworthy since it acts as a bi-, ter-, quadri-, sexi-, and septivalent element. Manganese also forms an unusual number of definite oxides, more indeed than any other element.

Manganous oxide, MnO	Basic, forms manganous salts
Mangano-manganic oxide, Mn_3O_4	Neutral or mixed oxide: probably a salt
Manganese sesquioxide, Mn_2O_3	Basic, forms manganic salts
Manganese dioxide, MnO_2	Basic dioxide and acidic; forms manganites
Manganese trioxide, MnO_3	Acidic, forms manganates
Manganese heptoxide, Mn_2O_7	Acidic, forms permanganates

Atomic weight.—Analyses of manganese chloride and bromide, silver permanganate, roasting manganous sulphate to oxide, and reducing manganese sulphate to manganese sulphide in a stream of hydrogen sulphide, all show that the combining weight of manganese (oxygen = 16) lies between 54·925 and 55·014; the best representative value is taken to be 54.93. This agrees with the estimation of the atomic weight by Dulong and Petit's rule.

Relation of manganese to the halogens.—Manganese does not form a family group with other elements with similar characters, as is the case with the halogens. Manganese, however, is usually classed with the halogens, but there are not many common properties between them. The similarity between the halogens and manganese virtually begins and ends with compounds of the highest oxide, Mn_2O_7, which itself is strikingly like Cl_2O_7. The corresponding acids are both monobasic, powerful oxidizing agents, and form isomorphous salts. There is a very great contrast between the lower oxides of chlorine and manganese, and between the elements chlorine and manganese. The relationship between chromium, manganese, and iron is much closer. Thus the isomorphism of the manganites and chromites; the isomorphism between the manganic and ferric alums, etc. The metals chromium, manganese, and iron also have many similar properties.

Uses.—Manganese dioxide is used as an oxidizing agent; in the manufacture of chlorine and bromine. It is used in decolorizing glass stained a yellowish tinge by the traces of "ferric silicate" present, for the violet colour of manganese silicate masks the complementary yellow tint of the iron. Manganese dioxide is also used as a "drier" for paints and varnishes; as a depolarizer in battery cells; colouring pottery bodies and glazes; etc. Wad is used in the manufacture of paint. A crude mixture of sodium manganate and permanganate is made by fusing sodium hydroxide with pyrolusite, and sold as a disinfectant under the name "Condy's fluid." Its "disinfecting" qualities depend upon its oxidizing properties.

Manganese is used in the manufacture of manganese bronze (*q.v.*), and also in the manufacture of iron and manganese steel. Manganese alloyed with iron, ferro-manganese, can be made by reducing the oxides with

carbon in an ordinary blast furnace, or in an electric furnace. Ferro-manganese is used for reducing the iron oxide formed in the Bessemer's converter, and for counteracting the deleterious effects of phosphorus and sulphur The resulting manganese oxides pass into the slag Since ferro-manganese contains about 4 or 6 per cent of carbon, it is used for re-carbonizing Bessemer's steel. Manganese steel is particularly hard and free from air blebs It is used in the manufacture of burglar-proof safes, *dredge pins*, shoes and crusher plates for ore mills, etc Cupro-manganese is an alloy of copper and manganese made by reducing the oxides of these metals in a graphite crucible or reverberatory furnace. F. Heusler's alloys (1903) contain copper, aluminium, and manganese (55 : 15 : 30) They are magnetic

Magnetic properties of the metals.—It is usual to regard iron, cobalt, and nickel as being particularly endowed with the magnetic quality, and Isaac Newton apparently believed that other bodies were quite uninfluenced by a magnet Faraday and Tyndall, on the other hand, have said that it is doubtful if any substance is totally unaffected by a magnet True enough, iron, cobalt, and nickel form a special group in that they acquire an enormous magnetization in comparison with other substances Excluding the three elements just mentioned, there is no sign of any permanent magnetization with the other elements, and a feeble magnetic effect can be induced only with difficulty The facts are here in agreement with the idea suggested by A. Schuster (1903). Every physical property hitherto discovered for one element has been found to be shared by all the others in varying degrees While cobalt, nickel, iron, and Heusler's alloys are attracted by the poles of a magnet; graphite, bismuth, and several other bodies are repelled. M. Faraday (1845) called the former paramagnetic bodies (παρά, beside), and the latter diamagnetic bodies (διά, across), because, when a rod of metal is suspended between the poles of a magnet, a paramagnetic body sets itself axially along a line joining the two poles, and a diamagnetic body sets itself equatorially, i e. at right angles to the line joining the poles Arranging the elements in two classes

Paramagnetic elements	K, C, Ti Ca N, O, Cr, U, Mn, Fe, Co, Ni, Rh, Pd, Os, Ir, Pt
Diamagnetic elements	H, Na, Cu, Ag, Au, Zn, Cd, Hg, Tl, Si, Sn Pb, P, As, Sb, Bi, S, Se, Cl, Br

No connection between the chemical and magnetic qualities of the elements have been detected. Elements so much alike as potassium and sodium, oxygen and sulphur, nitrogen and phosphorus, titanium and silicon, are separated in different classes The paramagnetic power of iron, cobalt and nickel decreases with increasing atomic weight, while with phosphorus antimony, and bismuth, and with copper, silver, and gold the paramagnetic power increases with increasing atomic weight

Questions

1 Given a solution of potassium permanganate, explain how the following substances can be obtained with its aid —manganese dioxide, manganese sulphate, chlorine, oxygen —*London Univ*

2 Explain the term "available oxygen" as applied to potassium permanganate and potassium dichromate respectively; also "available chlorine" as applied to bleaching powder —*London Univ*

3 What facts have led to the supposition that manganese is a heptad metal ?—*London Univ.*

CHAPTER XXVI

Iron, Nickel, and Cobalt

§ 1 Iron—Occurrence, Preparation, and Properties

History—Several fabulous stories have been told describing how meteoric iron falling to the earth was sent from heaven as a gift of the gods to man Iron implements have been used from prehistoric times one was found during some blasting operations in the pyramid at Gizeh (Egypt) which is probably 5000 years old In olden times, iron was symbolized by ♂, the spear and shield of Mars—the god of War—probably in allusion to its use in making weapons of war The methods for extracting and working iron were probably discovered later than those for copper and bronze Iron is frequently mentioned in the sacred writings The process of smelting iron is supposed to have originated in the East and the Hindoos acquired considerable skill in the manufacture of wrought iron The method of smelting by means of the blast furnace is said to have been introduced in Germany about 1350, and in Great Britain about 1500 Charcoal was first used as the reducing agent, in 1618 D Dudley commenced using coal, and in 1713 Darby used coke Coke and coal gradually displaced the use of charcoal Some charcoal is still used when wood is cheap, *e g* in a few places on the Continent and in America

Occurrence.—Small quantities of metallic iron occur in some basaltic rocks An unusual mass, over 25 tons has been found on the Disko Island, Greenland Since iron rapidly corrodes when exposed to a humid atmosphere, native iron is not at all common Nearly all meteorites contain iron associated with other metals—chiefly copper, cobalt and nickel Ferric oxide, Fe_2O_3, is widely distributed in nature as *red hæmatite*, red ore, or specular iron ore *Brown hæmatite* represents a class of hydrated oxides which may be represented by the general formula $Fe_2O_3.nH_2O$, where n represents the variable amount of water in different varieties—*limonite* is generally taken to be $Fe_2O_3.3H_2O$, that is, $Fe(OH)_3$, *göthite*, $Fe_2O_3.H_2O$, and *bog iron ore* which occurs in Ireland belongs to this class *Magnetite*, Fe_3O_4 is also called loadstone, and magnetic oxide of iron *Siderite*, $FeCO_3$, is a ferrous carbonate *Iron pyrites* FeS_2, and *chalcopyrites* or cupriferous pyrites, $CuFeS_2$, are not worked directly for iron on account of the difficulty involved in eliminating sulphur from the product Very few clays, soils, and granite rocks are free from small quantities of iron Iron plays an important part in the nutrition of higher animals and plants, since this element seems necessary for their healthy growth

Preparation and Properties—Commercial iron always contains small quantities of graphite, iron carbide, iron phosphide, iron silicide, iron

sulphide, and the corresponding manganese compounds "Electrolytic iron" is made by the electrolysis of a salt of iron—ferric sulphate, and almost pure iron can be made by reducing a salt of iron—oxalate, chloride, or oxide—in a stream of hydrogen gas at 500° to 600° If the reduction be carried out at a lower temperature, the black powder may become incandescent on exposure to the air—pyrophoric iron Pure iron crystallizes in the cubic system, Fig 171 Iron is a grey, lustrous metal, it melts at 1500° and boils at 2950° If a polished surface of a piece of iron be magnified about 150 diameters, a series of boundary lines between the crystal walls appear as indicated in Fig 172 The boundary lines are irregular because the crystals of the mass have been too closely packed together to enable them to develop their characteristic shape For convenience, the pure metal is sometimes called ferrite

Allotropic forms of iron—If the temperature of a cooling bar of almost pure iron be recorded every half minute by a recording pyrometer the cooling process does not appear to be uniform and continuous, because the metal cools down to about 860°, and then becomes hotter, the cooling is then resumed until, at about 750°, the temperature again begins to oscillate These temperature fluctuations are supposed to be due to the transition of iron from one allotropic modification to another Each transition temperature corresponds with a change in the mechanical and physical properties of the iron The sequence of changes is reversed when the cold iron is heated. Iron below 680° is called α-ferrite, between 750° and 860°, β-ferrite, and above 860°, γ-ferrite. If the iron contains some carbon in solution, both the transition points approach 720° The proximity of these points to 720° depends on the amount of carbon in solution A new disturbance then appears in the cooling curve at about 660° There is a marked evolution of heat at this temperature, for the red-hot cooling steel glows more brightly than before. This phenomenon was called by its discoverer—Barrett (1874)—the recalescence of steel. Some consider β-ferrite is a solid solution of γ-ferrite in α-ferrite.

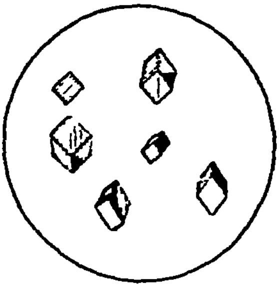


Fig 171 —Cubic Crystals of Iron

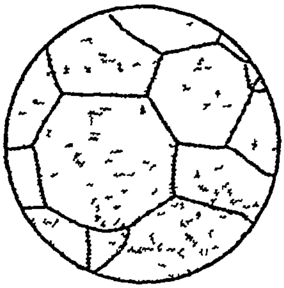


Fig 172 —Ferrite

The action of acids—Iron dissolves in dilute acids, sulphuric acid furnishes ferrous sulphate and hydrogen, and hydrochloric acid furnishes ferrous chloride and hydrogen With cold dilute nitric acid, hydrogen is not evolved but the acid is reduced to ammonia, and this reacts with the excess of nitric acid to form ammonium nitrate With hot nitric acid, ferrous nitrate and nitrogen oxides are formed. With concentrated nitric acid (specific gravity 1 45), the iron does not dissolve The iron in contact with the concentrated acid appears to have changed, for it behaves differently from a piece of the same sample of iron which has not been in contact with concentrated nitric acid The sample which has not been in contact with the strong acid will precipitate copper from copper sulphate solutions, lead from lead nitrate, and silver from silver nitrate, the

other sample will not. The inert iron is said to be in the passive condition. Passive iron does not dissolve when dipped in dilute nitric acid. Other oxidizing agents, chromic acid, hydrogen peroxide, will make iron passive. Chemists are not yet agreed as to the cause of passivity; the general idea is that a thin film of oxide is formed on the metal by contact with the oxidizing agent. The passivity can be removed by scratching the surface of the iron, by heating it in a reducing gas, by strongly rubbing the surface, and by bringing the passive iron in contact with zinc while immersed in the dilute nitric acid. Other metals also exhibit passivity, *e.g.* cobalt, nickel, chromium, and bismuth.

The rusting of iron.—When commercial iron is exposed to a humid atmosphere for a short time, it soon becomes covered with a reddish brown film which is called *rust*. Iron rust seems to be an indefinite mixture which on analysis furnishes numbers which vary according to the age of the rust, etc. Rust usually contains ferrous oxide, ferric oxide, carbon dioxide, and water. Analyses show that rust is probably a mixture of ferric oxide, hydrated ferrous and ferric oxides, and basic ferrous and ferric carbonates. If the rust has been long exposed to the air, the amount of ferric oxide is relatively large, and the amounts of ferrous oxide and carbon dioxide small. Rusting is a complex process, and workers are by no means agreed on the simple facts. Dry iron in dry air does not rust; moisture must be present before rusting can occur. Some deny, others affirm, that the presence of an acid and water are necessary. It is exceedingly difficult to free water and the surface of glass from carbon dioxide; and silicic acid can be dissolved from the glass vessels used and from particles of slag in the iron. However, where careful attention has been taken to eliminate the disturbing factors, the evidence seems in favour of the conclusion that the presence of an acid is necessary for rusting; that an acid is always present when the iron dissolves; and it is highly probable that pure iron does not undergo appreciable oxidation when exposed to pure water and to pure oxygen. Films of moisture frequently condense on the surface of iron exposed to the air, and the moisture holds carbonic acid and oxygen in solution. The mechanism of the "atmospheric rusting" of iron may then proceed according to the following scheme. An acid ferrous carbonate, $Fe(HCO_3)_2$, or a basic carbonate, $Fe(OH)(HCO_3)$, is first formed. The ferrous carbonate in contact with oxygen is oxidized to basic ferric carbonate, $Fe(OH)_2(HCO_3)$, or to $Fe(OH)(HCO_3)_2$, or both. The basic ferric carbonate is then hydrolysed by the water forming ferric hydroxide, $Fe(OH)_3$, and the ferric hydroxide is subsequently more or less dehydrated, forming ferric oxide. Ferric oxide is more or less hygroscopic, so that once rusting has started, at any point, subsequent corrosion is quicker because the ferric oxide helps to keep the surface of the iron adjacent to the rust spot moist. Several other hypotheses have been suggested, and the subject is still *sub judice*.

Atomic weight.—The combining weight of iron determined by the analysis of the chloride, bromide, and iodide, and the synthesis of the oxide furnish numbers between 55.84 and 56.23 (oxygen = 16); and 55.85 is taken to be the best representative value. This agrees with the atomic weight deduced from the vapour density of the volatile compounds of iron; and by Dulong and Petit's method of approximation—specific heat of iron, 0.110.

§ 2 The Manufacture and Properties of Pig Iron.

The blast furnace for iron is the most efficient metallurgical instrument that exists —W M JOHNSON (1914)

The oxides and carbonates are the sources of commercial iron These ores frequently contain a certain amount of clay, and the ores are then termed *clay ironstone* The so-called *black band ironstone* is a ferrous carbonate contaminated with clay, and black coaly matters The clay ironstones are usually calcined or roasted by stacking the ore with a small quantity of fuel in heaps, in stalls, or in shallow kilns In the former case, combustion is started at one point and allowed to proceed throughout the whole mass The temperature of the smouldering mass is sufficient

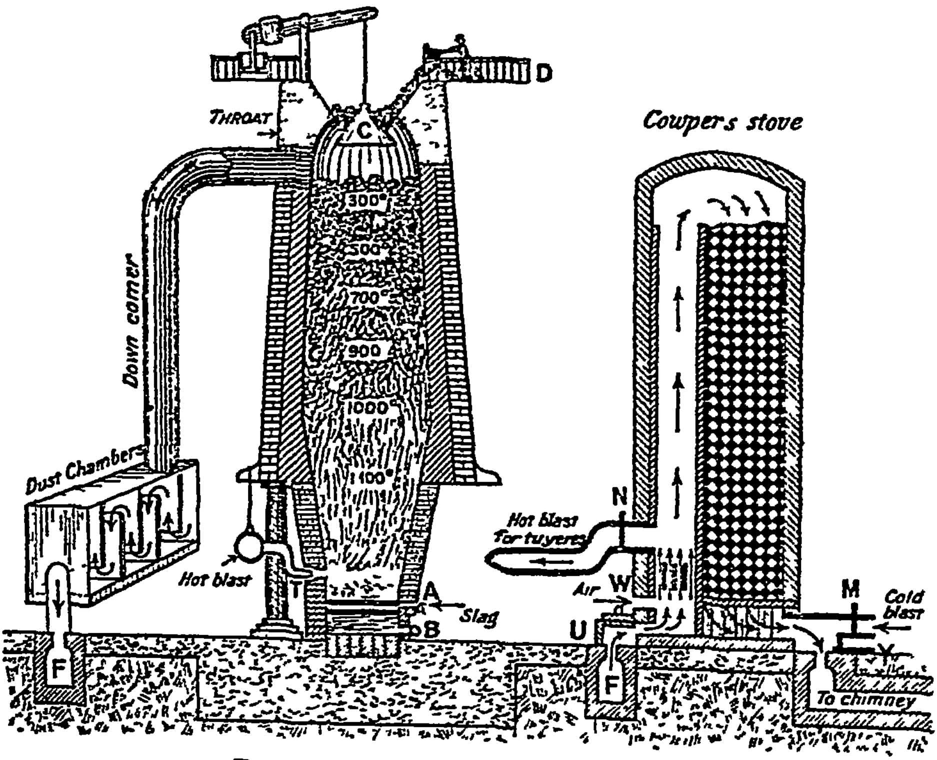


FIG 173 —Blast Furnace (Diagrammatic)

to drive off most of the moisture, and carbon dioxide, and burn the organic matter and some of the sulphur and arsenic The ferrous oxide is also oxidized to ferric oxide This prevents the early formation of a fusible slag which would attack the lining of the furnace Ferric oxide does not form a slag at so low a temperature as ferrous oxide At the same time the ore is made somewhat porous, and this facilitates its reduction to metallic iron at a later stage of the process

The reduction of the calcined ore or of ferric oxide is effected in a blast furnace The blast furnace is a long cylindrical shaft fed with ore, fuel and flux at the top, and supplied with the air necessary for the combustion of the fuel at the bottom The function of the blast furnace is to reduce the iron oxides to the metallic condition, and to free the iron so reduced

from earthy admixtures by forming a slag which is fusible at the temperature of the furnace. The molten iron and slag are discharged at the bottom of the furnace, and the gases pass away at the top.

The blast furnace.—The smelting, as just indicated, is conducted in a tall cylindrical furnace—say 80 feet high—and shaped approximately as indicated in the section, Fig. 173. The dimensions and constructional details of blast furnaces vary somewhat in different localities. The furnace now being described has an outer shell made of iron plates riveted together. Inside this is a casing of ordinary brick work, and inside this a lining of firebricks—1½ feet thick. The parts which are subjected to the greatest heat are built independently so as to facilitate repairs. The greatest internal width is 20 feet. This part is called the *bosh*. The mouth of the furnace is closed by a single usually double *cup-and-cone feeder*, *C*. The materials for charging the furnace are conveyed in trucks to the *charging gallery*, *D*, at the top of the furnace, and there tipped into the cup of the feeder. When the cup is filled, the cone is depressed, and the charge automatically distributed in the interior of the furnace. The waste gases pass away *viâ* the outlet at the throat of the furnace. The furnace narrows below the boshes and at the hearth the diameter is 8 feet. Molten iron and slag collect on the hearth, and outlets are here provided: one *A* for tapping the slag, and another *B*, for tapping the iron. Between 6 and 8 feet from the base of the furnace six openings, *T*, are provided for the insertion of water-cooled nozzles—*tuyeres*—through which a blast of hot air is forced into the furnace.

The hot gases from the top of the furnace are led down a flue—the *down-comer*—into a chamber—the *dust-catcher*. The gases pass from the dust catcher along an underground flue, *FF*, to a tower—*Cowper's stove*—packed checkerwise with fire bricks. The flue gas is burnt in the combustion chamber of the stove and the products of combustion pass on to the chimney. The secondary air required for the combustion of this gas enters through the ports, *W*. The burning gas raises the temperature of the checker brick work. When the temperature of the stove is hot enough the gases from the blast furnace are deflected and burnt in an adjoining similar tower; meanwhile the gas and air valves—*U*, *V*, *W*—in the hot tower are closed; and another set of valves—*M*, *N*—connecting the tuyeres with the blowing machine are opened. The cold air passing through the hot checker work of the Cowper's stove on its way to the tuyeres is heated. When the tower has been cooled sufficiently the adjoining stove is hot. The gas from the blast furnace is again burned in the cooled tower and the blast is sent through the hot tower. Thus the towers are alternately heated by the combustion of the gas from the blast furnace, and cooled by the cold air from the blowing machine. In this way the blast of air is heated.

The reactions in the blast furnace during smelting.—The chemical changes which take place in the blast furnace during the smelting of iron ore are somewhat complex. Hence the following sketch must be regarded as a simplified description.

1. **The ore.**—The ore, mixed with coke and limestone, is exposed, in the upper part of the furnace, to the action of reducing gases, principally carbon monoxide, ascending from the lower part of the furnace. The action commences between 200° and 500°, that is, as soon as the charge has commenced its downward descent: $Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2$; and reduction continues with increasing velocity as the charge descends into the hotter part of the furnace. Most of the oxide is reduced before it has descended 10 feet below the level of the charge; any oxide which has escaped reduction will then be reduced by the carbon: $Fe_2O_3 + 3C = 3CO + 2Fe$. The hot spongy iron meets the ascending carbon monoxide, and decomposes part: $2CO = CO_2 + C$. The solid carbon is deposited amidst the spongy iron. The iron undergoes little change until it reaches the zone of fusion. The iron, however, absorbs or dissolves much carbon as it passes down the furnace. The melting point of a

mixture of iron and carbon is lower than that of pure iron, so that while the temperature of the blast furnace would not be sufficient to melt pure iron to the necessary fluid condition, the temperature required for iron with carbon in solution is easily maintained The molten iron trickles down and collects in the well of the furnace below the tuyeres The iron takes up many other elements in addition to carbon during its descent in the furnace Thus, silicon, sulphur, phosphorus, and manganese are partly absorbed by the iron, and partly by the slag

2 The ascending gases —The oxygen of the hot air blast burns the carbon of the hot coke $C + O_2 = CO_2$, and the carbon dioxide is at once reduced by the hot carbon $CO_2 + C = 2CO$ The ascending gases warm up the descending charge When the temperature reaches about 600°, the limestone begins to decompose $CaCO_3 = CO_2 + CaO$ Most of the carbon dioxide thus formed is at once reduced by the excess of carbon to carbon monoxide At this stage, the reduction of the iron oxide to spongy metallic iron is practically complete An excess of carbon monoxide is needed for the reduction because the reaction, $Fe_2O_3 + 3CO \rightleftharpoons 3CO_2 + 2Fe$, is reversible, and a condition of equilibrium would be attained when only a certain proportion of the ferric oxide is reduced An excess of carbon monoxide favours a more complete reduction of the ferric oxide There are quite a number of concurrent reactions taking place at the same time If any water is present in the blast, it will be reduced: $H_2O + C = CO + H_2$, and the nitrogen of the air, brought in with the gas, forms a little cyanogen The net result is a combustible gas, containing approximately

CO	CO_2	N	H	Hydrocarbons
25 3	10 5	58 1	4 3	1 6 per cent

The combustible gas is utilized for heating the blast and if there be any surplus, it is used for heating the boilers which run the blowing engine, for calcining the ore, and for general heating purposes If coal be used in place of coke, tar, etc, separate from the gas at the base of the downcomer by the process described under coal gas

3 The slag —When the charge in the furnace has descended about 20 or 30 feet, and the temperature is about 600°, it has formed a mixture of spongy iron, earthy gangue, coke, and limestone or quicklime Little further change occurs until the temperature is hot enough to melt the mixture At this temperature, a fusible slag is formed containing approximately 55 per cent SiO_2, 30 per cent CaO, and 15 per cent Al_2O_3 The fused slag trickles down into the well, and floats on the surface of the molten iron The slag is drawn from the furnace at intervals, and, when cool enough, tipped on the slag heap The slag is derived from the ash of the fuel, from the earthy gangue of the ore, and the fluxes added with the charge to promote fusion The composition of the slag varies with the quality of the iron, etc Success in working the blast furnace depends largely upon the nature of the slag Some types of slag which do not disintegrate on exposure to the air are used as road metal, and railway ballast, or mixed with some clay and moulded into bricks for paving, and building purposes Some varieties of slag are made into cement

The properties of pig iron —The molten metal which collects in the well is tapped at intervals—say twice every twenty-four hours, and run

into sand moulds, or into "chilled moulds," and allowed to solidify. The iron is then called pig iron. The "pigs" of iron are about 3 feet long, and 3 or 4 inches thick. In some cases the molten metal is run directly into a mixer, or into Bessemer's converter and made into steel. Ore, flux, and coke, enter the furnace; molten iron, molten slag, and gaseous products leave the furnace. Fresh charges of ore, coke, and flux, are added in definite proportions at regular intervals, and the smelting of the ore thus continues without interruption for months or years.

The pig iron is classed according to its quality. Ordinary pig iron contains from 1.5 to 4.5 per cent. of carbon. Higher proportions are sometimes present when the raw materials contain much manganese or chromium. The carbon of pig iron occurs in at least two different states —free and combined. Combined carbon is either in solution, or present as a definite chemical compound, see "Steel." The mode in which the carbon is associated with the iron has a marked effect on its properties. The free carbon, interspersed as graphite through the pig iron, is well shown on the fractured surface of a broken pig. If pig iron be digested with hydrochloric acid, the graphite remains behind as an insoluble black powder, but the combined carbon unites with the hydrogen forming various hydrocarbons which colour the solution yellowish brown, and give the escaping gas a characteristic unpleasant smell. The gas is also contaminated with hydrogen sulphide, silicide and phosphide derived from the impurities—iron sulphide, silicide, and phosphide—in the iron. The classification of pig iron is based on the relation of free to combined carbon. If much of the carbon be "free," the iron is called **grey pig iron**; and if much combined carbon be present, **white pig iron**; intermediate varieties are called **mottled pig iron**. The grey and mottled varieties are further subdivided. Pig irons too are often graded according to their source because certain districts work a specially pure or a specially foul ore, and thus gives the iron from these districts characteristic properties. The following analyses will illustrate the difference between the three varieties of pig iron:

	Grey	Mottled	White
Combined carbon (C.C.)	0.90	1.80	3.00 per cent.
Free carbon (Gr.)	2.8	1.40	0.10 per cent.

The pig iron also contains silicon, sulphur, phosphorus, and manganese. Cast or pig iron is not malleable, nor can it be welded. It is used for casting articles—like stoves and ornamental iron—which are not likely to be subjected to shocks. Cast iron is the starting point for the manufacture of wrought iron and steel.

§ 3. The Manufacture and Properties of Wrought Iron.

Wrought iron is made by melting pig iron with "scrap" iron on the bed of a reverberatory furnace, Fig. 174, lined with iron ore (Fe_2O_3). The reverberatory furnace—here called a *puddling furnace*—was first used for iron by T. and G. Cranage in 1776, and more successfully by H. Cort in 1784, although similar furnaces had been used by copper smelters for some time. Rogers, in 1816, improved the furnace by introducing a bed of iron oxide in place of siliceous matters previously used. Part of the carbon, silicon, sulphur, and phosphorus of the cast iron are oxidized by the furnace lining,

and the metal melts to a fluid mass on the bed of the furnace (*melting stage*) The puddler then thoroughly mixes the charge so as to bring the molten metal into intimate contact with the iron oxide of the furnace bed The puddler works the iron through an opening in the side of the furnace The sulphur, phosphorus, and silicon are partly oxidized Jets of flame soon appear on the surface of the molten metal—"puddler's candles" (*fluid stage*) The carbon is oxidized to carbon monoxide which burns to carbon dioxide The other impurities are also partly oxidized, and form a slag with the lining of the furnace (*boiling stage*) The iron then becomes "pasty" because purified iron melts at a higher temperature than the less pure iron The molten mass is stirred, puddled, and finally gathered into large "balls" or "blooms," each ball about 80 lbs in weight (*balling stage*) The balls are removed from the furnace, and squeezed nearly free from slag by working under a steam hammer The iron is then rolled into sheets so as to give the finished product a fibrous structure.

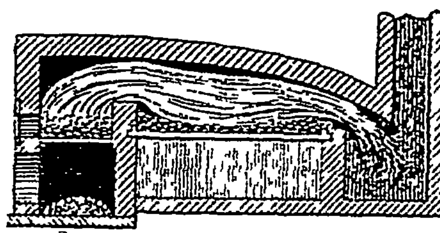


Fig 174 —Puddling Furnace (Diagrammatic)

While cast iron melts at about 1200°, wrought iron melts at about 1550° Wrought iron softens at about 1000°, and it can then be forged and welded Wrought iron is tough and malleable, and fibrous in structure, cast iron is brittle, and it has a crystalline structure Wrought iron can be rolled into plates and drawn into wire It is made into wire, nails, chains, anchors, horseshoes, agricultural implements, etc It is not used so much as formerly, because it has been largely replaced by steel When heated red hot and quenched in cold water, wrought iron does not harden, steel under the same treatment becomes very hard.

§ 4 The Manufacture of Steel—Crucible and Cementation Processes.

The amount of carbon in steel is usually intermediate between that in cast iron and in wrought iron Steel is made by decarbonizing cast iron, or by carbonizing wrought iron The latter process gives the more reliable result because wrought iron is less contaminated with other impurities The principal methods of making steel are (1) the cementation process, (2) the crucible process, (3) electric processes, (4) Bessemer's acid and basic processes, and (5) Siemens and Martin's acid or basic processes

The cementation process —Bars of specially pure varieties of wrought iron—*e g* Swedish iron—are packed with charcoal in boxes made of fire-brick, and sealed with a lute of refuse from the troughs below the grind-stones of the steel grinders The boxes are heated in a furnace for 8 to 11 days at about 1000° The time and temperature depend upon the amount of carbon to be incorporated with the wrought iron The bars, when removed from the cold furnace, have a blistered appearance, hence the term *blister steel* The bars are broken and sorted by experts who estimate the quality from the appearance of fractured surfaces The blistered steel is then heated, and hammered into bars. The product is a high-class tool steel called *shear steel* The only change in composition which

can occur during the cementation is due to carbon, and some of the purest steels in commerce are made by this process. Blister steel is also melted in crucibles and cast into ingots for high grade cast steels. The cementation process is being gradually displaced by cheaper processes.

During cementation, solid carbon slowly diffuses into the iron. Probably at the high temperature, gaseous carbon compounds play some part in the action. May be carbon monoxide is formed and occluded by the iron. The carbon monoxide is then decomposed $2CO = CO_2 + C$. The carbon dioxide escapes into the box of charcoal and there forms more carbon monoxide. This is again occluded by the iron, and the cyclic action $CO \rightarrow CO_2 \rightarrow CO \rightarrow$ is repeated indefinitely. Possibly also some cyanogen compounds take part in the action.

The crucible process for cast steel.—Bars of wrought iron are melted with a definite amount of carbon in fireclay crucibles. The iron slowly changes into steel by absorbing carbon. The time required is about four hours. Experience has taught the melter how much charcoal is needed to bring the metal up to the required carbon content. The success of the operation depends upon the skill in the selection of the iron, in the adjustment of the charge, and on careful melting. Crucible steel is usually a high grade tool steel used for razors, files, etc. A less pure product is made by heating a mixture of wrought iron with the necessary amount of cast iron. High grade crucible steel is more expensive than Bessemer or open hearth steel. The term "cast steel" was originally reserved for crucible steel, but the cognomen is sometimes applied by vendors to steels made by cheaper processes.

Special steels of the self hardening type are usually made by the crucible process, by alloying steel with small quantities of other metals, these impart hardness toughness, and strength. In districts where electric power is cheap, electric furnaces are coming into use for the manufacture of steel. Electric furnaces may not succeed in ousting the Bessemer and open hearth processes, but they promise to play an important part in the future of the steel industry, and possibly may displace some of the older processes of making special steels.

§ 5 The Manufacture of Steel—Bessemer's Process

In 1852, Kelly patented a process for purifying pig iron, based on the fact that if air be forced through a mass of molten pig iron, in a suitable vessel, the impurities which prevent the pig iron being ductile and malleable are removed, and a bath of molten metal, virtually wrought iron, is obtained. In 1856 H. Bessemer patented a converter suitable for the process. Bessemer afterwards bought Kelly's patents. The metal in the converter can be mixed with a known amount of spiegeleisen—i.e. a ferro manganese containing a known amount of carbon. The steel is then at a sufficiently high temperature to permit of its being cast into moulds. By this wonderful process, in half an hour's time, 10 tons of steel can be prepared at but a small fraction of the cost of manufacture by the processes which precede. This method of making steel has virtually revolutionized the art.

In Bessemer's process about 10 tons of molten pig iron are run into a large egg shaped vessel, called the *converter*. The converter can be tilted into any required position. It is provided with holes at the bottom through which a powerful blast of air can be blown. The converter is made of wrought-iron plates, and lined with a bed made of silica and clay. A general

idea of the structure of a converter can be gathered from Fig 145, which shows part of the inside and part of the outside Molten pig iron is run into the converter, and a powerful blast of air in fine jets is forced through the mass of molten metal The temperature rises owing to the heat evolved by the oxidation and combustion of the impurities—the carbon, sulphur, and manganese The carbon forms carbon monoxide which burns at the mouth of the converter The flame is accompanied by a brilliant shower of sparks The other oxides form a slag with the furnace lining Experience and the appearance of the flame tells the operator when to stop the blast The right amount of spiegeleisen is then added to make a metal of definite composition The blast is again turned on for a moment, and the metal is then cast into moulds to form blocks of Bessemer's steel

Thomas and Gilchrist's basic process —The sulphur and phosphorus are not removed by Bessemer's process just indicated. In 1878 S G Thomas and P C Gilchrist showed that, if the converter be lined with, say, dolomite (basic lining), and some lime be added to the charge of pig iron, and the blast continued a little longer, the oxides of phosphorus, sulphur, and silicon formed are absorbed by the furnace lining The operation is otherwise conducted as before The lining, after use, is called *Thomas' slag*, and it is used as a fertilizer on account of the phosphorus it contains If the lining is siliceous, the operation is called the *acid Bessemer's process*, and if the lining be dolomite, the *basic Bessemer's process*

§ 6 The Manufacture of Steel—Siemens and Martin's Open Hearth Process

E Martin (1864) made steel by fusing pig iron admixed with wrought iron scrap in an open sand basin, and W Siemens (1863) by treating pig iron and pure hæmatite ore in a similar manner The idea thus originated with the latter, though the process is usually called the "Siemens-Martin" process, or the open hearth process. In this process, the furnace is charged with a mixture of pig iron, scrap (wrought) iron, and good hæmatite ore free from carbon The mixture is melted in a shallow rectangular trough or hearth The furnace is heated by producer gas. Both the gas and the secondary air for the combustion of the gas are pre-heated so that a very high temperature can be obtained A general idea of the process can be gathered from Fig 175, which shows a section through the hearth The air port is not shown in the diagram The gas and air burn on the left, the flue gases travel down the flue on the right, and in doing so heat up two chambers below The direction of the burning gas is then reversed Gas and air pass separately through the hot chambers, and the flue gases heat up another pair of chambers below the hearth The direction travelled by the burning gas is reversed about every half hour, and the heat of the flue gases is utilized in warming up chambers through which the unburnt gas and air will pass later on The furnace is called *Siemens' regenerative*

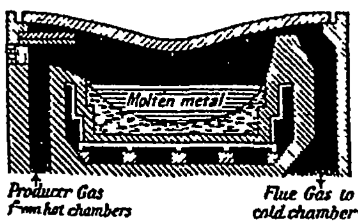


FIG 175 —Hearth of Siemens-Martin's Process (Diagrammatic)

furnace When a test shows that the metal contains the right amount of carbon, ferro manganese is added as in the case of Bessemer's steel If the bed of the furnace is made of siliceous materials—*acid process*—the proportion of carbon, silicon, and manganese are reduced during the treatment, but the amounts of sulphur and phosphorus remain fairly constant In the *basic process*, the furnace is bedded with, say, dolomite, and there is a steady fall in the amount of phosphorus and sulphur during the treatment, just as was the case with the basic Bessemer's process of Thomas and Gilchrist

§ 7 The Constitution and Properties of Steel

It may be said in a rough kind of way that steel is intermediate between cast and wrought iron so far as the proportion of carbon is concerned. Thus,

	Pig iron	Steel: Hard	Steel: Medium	Steel: Soft	Wrought iron
Carbon (per cent)	3 0	0 9	0 4	0 1	0 06

but some of the so called carbonless steels contain less carbon than wrought-iron, and there are no hard and fast boundary lines Indeed, it does not seem possible to define steel satisfactorily without reference to its mode of manufacture Iron at about 1240° can dissolve 5 per cent of carbon, the amount dissolved increases with the temperature. A sample of iron of 99 98 per cent purity melted at about 1600°, and the freezing point of iron is lowered by the presence of carbon in the same way that the freezing point of water is lowered by salt (Fig 55) The freezing point curve for solutions of carbon in iron is shown in Fig 176 If a molten saturated solution of carbon in iron be slowly cooled, the excess of carbon separates as graphite, and the still molten mother liquid becomes poorer in carbon , as the temperature falls, graphite continues separating as illustrated by the curve *BO*, Fig 176 When the mother liquid has 4 3 per cent of carbon in solution, it solidifies *en masse* at 1130°, corresponding with the point *O* The mixture containing 4 3 per cent of carbon is the most fusible mixture of carbon and iron—the eutectic mixture, and 1130° is the eutectic temperature If the cooling fluid contains less than 4 3 per cent of carbon, a solid solution of about 2 per cent of carbon commences to separate, and continues separating as the solution cools until the remaining fluid has the eutectic composition, which solidifies *en masse* at 1130° Remember that iron above 860° is in the γ condition , and between 860° and 750° in the β condition The solid solution of carbon in γ ferrite above 860° is called austenite—after W C Roberts Austen , and the solid solution of carbon in β ferrite, martensite—after A Martens α ferrite does not appear to form a solid solution of carbon in the same way as do β and γ ferrite

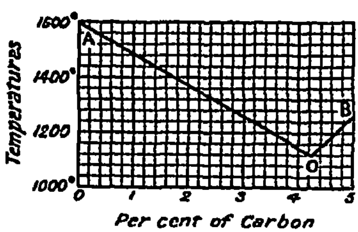


FIG 176 —Freezing Curves of Carbon Iron Solutions

J O Arnold calls a solid solution of iron with 0 89 per cent of carbon, hardenite. Hardenite has a constant composition 0 89 per cent carbon This may correspond with a definite carbide of iron, $Fe_{24}C$, or possibly with

a solution of iron carbide, Fe_3C, in iron $Fe_3C + 21Fe$ In any case, if hardenite be cooled slowly, it decomposes just below 700° into a mixture of ferrite (iron) and cementite There is a marked evolution of heat during the decomposition of the hardenite This corresponds with the *recalescence* of cooling steel just below 700° Cementite is an iron carbide, Fe_3C, or a solid solution containing Fe_3C with traces of several other carbides The mixture of cementite and ferrite forms alternate layers of different degrees of hardness When the *surface of the metal* is polished the harder parts stand out in relief This gives the surface an appearance resembling mother-of-pearl Hence the mixture has been called "the pearly constituent of steel," or simply pearlite The alternate layers, *under the microscope*, have the appearance shown in Fig 177 If the solid solution—hardenite—be cooled so quickly that the décomposition products of the hardenite have not time to segregate into alternate layers, but produce a more or less ill-defined mixture of cementite and ferrite, the mixture is called sorbite—after H. C Sorby With slowly cooled steels the pearlitic structure is well developed, and with more quickly cooled steels, the sorbitic structure prevails. If the iron has less than 0 89 per cent of carbon, ferrite separates from the cooling solid solution until a mixture of ferrite embedded in a matrix of hardenite with 0 89 per cent of carbon remains, the hardenite then dissociates as indicated above Similarly, if the solution has more than 0 89 per cent. of carbon, cementite separates until a matrix of cementite imbedded in hardenite, with 0 89 per cent of carbon, is formed, the hardenite then dissociates as before It will be noticed that pearlite and sorbite are *not definite constituents*, the terms refer to the mode in which certain constituents of a mixture are aggregated together Metallographists are not all agreed in their interpretations of the observed phenomena, and details are still in the throes of disputation

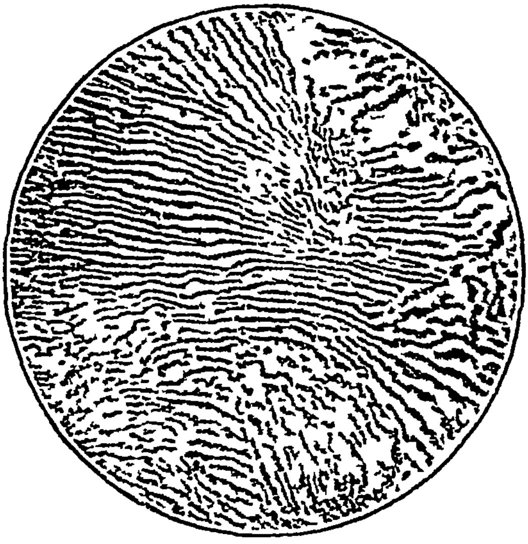


Fig 177 —Pearlite

The sudden quenching of the steel while these changes are in progress may arrest or inhibit further change Similarly, re heating followed by sudden quenching may completely alter the structure, and accordingly also the properties of the metal The hardness of steel thus depends upon its *composition and its history*—the way the metal has been cooled, and on its subsequent heat treatment. A typical steel containing nearly 1 per cent of carbon when heated to a high temperature and suddenly chilled, becomes so hard that it will scratch glass, and so brittle that it will not bend very far without breaking The operation is called hardening steel. The

hardenite of hardened steel is preserved more or less undecomposed when the steel is suddenly chilled—hence the term "hardenite" If the hardened steel be re heated to its original high temperature and slowly cooled—"letting down," or annealing steel—it becomes soft and ductile. By re heating hardened steel to certain definite temperatures—200° and upwards—and then cooling under definite conditions, steels can be obtained of varying, yet definite, degrees of hardness and ductility This has been traced to changes in the constitution of the metal The process of re-heating a hardened steel to a temperature far short of that employed when the steel was hardened is called tempering steel

§ 8 Iron, Nickel, and Cobalt Monoxides

Ferrous oxide, FeO—Ferrous oxide is formed as a crystalline, black, magnetic substance when carbon dioxide is reduced by hot metallic iron Ferrous oxide appears to be an intermediate stage in the reduction of ferric oxide by hydrogen or carbon monoxide, and hence the product is likely to be contaminated with either the higher unreduced oxide, or with metallic iron Ferrous oxide is also formed when ferrous oxalate is heated out of contact with the air When exposed to the air, ferrous oxide is oxidized to ferric oxide, Fe_2O_3 White ferrous hydroxide, $Fe(OH)_2$, is precipitated when an alkaline hydroxide or ammonia is added to a solution of a ferrous salt, provided air be entirely absent, but if the solutions have dissolved air, the precipitate will have a greenish colour The white precipitate rapidly absorbs oxygen, and passes into ferric hydroxide, $Fe(OH)_3$. Ferrous hydroxide and oxide dissolves in acids, forming ferrous salts.

Cobaltous hydroxide, $Co(OH)_2$.—A basic cobaltous chloride, $Co(OH)Cl$, is formed as a blue precipitate when potassium hydroxide is added to a solution of a cobaltous chloride The basic salt, on boiling, is converted into rose red cobalt hydroxide, $Co(OH)_2$ This turns brown on exposure to the air owing to the absorption of oxygen The hydroxide dissolves in hot concentrated potassium hydroxide, but it crystallizes from the solution on cooling Cobaltous hydroxide thus shows feeble acidic properties The hydroxide dissolves in ammonia, forming "cobalt-ammine" compounds (*q v*) The ammoniacal solution rapidly absorbs oxygen from the air If cobalt hydroxide, carbonate, or nitrate be strongly heated in the absence of air, cobaltous oxide, CoO, is formed as a dark brown powder This oxide is stable in air, but when heated, it absorbs oxygen, and forms an oxide corresponding with cobalto cobaltic oxide, Co_3O_4 When heated in hydrogen or carbon dioxide, the cobalt oxides are reduced to metallic cobalt Both the oxide and the hydroxide dissolve in acids forming cobaltous salts

Nickelous oxide, NiO—When potassium hydroxide is added to a solution of a nickel salt, a pale green precipitate of nickelous hydroxide, $Ni(OH)_2$—approximately $4Ni(OH)_2.H_2O$ separates. Unlike ferrous and cobaltous hydroxides, this precipitate does not oxidize on exposure to the air It dissolves in ammonia and ammonium salts forming ammines, and, unlike the corresponding cobaltous compound, the solution does not absorb oxygen from the air If the hydroxide or carbonate of nickel be heated out of contact with air, a greenish powder of nickel oxide, NiO, is formed This oxide when heated in air forms nickel sesquioxide, Ni_2O_3

Both the oxide and hydroxide dissolve in acids, forming nickelous salts.

§ 9 Iron, Cobalt, and Nickel Sesquioxides

A voluminous reddish-brown precipitate of ferric hydroxide, $Fe(OH)_3$, is formed when ammonia is added to a solution of a ferric salt As in the case of aluminium hydroxide, $Al(OH)_3$, there is some doubt whether a real hydroxide is formed. Several hydrated hydroxides are said to have been obtained by drying the precipitate at different temperatures, or by precipitating the hydroxide under special conditions Some of the hydrates occur in nature For instance, *limonite* has a composition corresponding very nearly with $2Fe_2O_3.3H_2O$, *gothite*, $FeO(OH)$ or $Fe_2O_3.H_2O$, isomorphous with diaspore and manganite For "dialyzed iron," that is, a hydrosol of iron oxide, see p 254 Ferric hydroxide is a very weak base, and the ferric salts are hydrolyzed in aqueous solution The ferric oxide Fe_2O_3 occurs in nature as *specular iron ore*, which crystallizes in lustrous black crystals belonging to the hexagonal system, and in reddish masses of *hæmatite* isomorphous with corundum Ferric oxide is a reddish-brown powder formed when ferrous sulphate, or carbonate, or hydroxide, or many organic salts of iron are calcined in air It is stable at a red heat, but at temperature above about 1000° it decomposes into Fe_3O_4 The powdered ferric oxide formed as just described, is used as jeweller's polishing powder —rouge—and as a pigment. The particular tint of the pigment depends upon the temperature of calcination, which, in turn, appears to determine the size of the grains of the ferric oxide Both ferric oxide and the hydroxide are basic, and give rise to ferric salts when heated with acids Some of the native oxides, and the oxide which has been heated to a high temperature, dissolve in acids but slowly

Nickelic oxide, Ni_2O_3—This oxide is formed as a black powder when nickel nitrate or carbonate is ignited in air at a low temperature Nickelic hydroxide, $Ni(OH)_3$, is precipitated when chlorine is passed through water or alkaline hydroxide in which nickelic oxide is suspended, and also when a nickel salt is treated with a solution of bleaching powder Nickelic oxide and hydroxide do not appear to be basic oxides, for when treated with acids, nickel*ous* salts and oxygen or its equivalent are obtained Thus $Ni_2O_3 + 6HCl = 2NiCl_2 + 3H_2O + Cl_2$, and $2Ni_2O_3 + 4H_2SO_4 = 4NiSO_4 + 4H_2O + O_2$. Hence nickelic oxide is a basic peroxide like manganese dioxide When nickelic oxide reacts with ammonia, nitrogen is evolved and nickelous hydroxide is at the same time precipitated $Ni_2O_3 + 2NH_3 + O_2 = 2Ni(OH)_2 + H_2O + N_2$

Cobaltic oxide, Co_2O_3—Cobaltic oxide is obtained by heating cobaltous nitrate or carbonate in air It is a grey powder which forms an oxide corresponding with cobalto cobaltic oxide, Co_3O_4, when heated to redness Cobaltic hydroxide, $Co(OH)_3$, is formed as a black precipitate when a cobaltous salt is treated with alkaline hypochlorite Both the oxide and the hydroxide dissolve in acids forming brown solutions which contain unstable cobaltic salts, these salts decompose when warmed, forming cobaltous salts and oxygen or its equivalent Hence cobaltic oxide behaves as a feebly basic oxide and as a peroxide like nickelic oxide and manganese dioxide

§ 10 The Higher Oxides of Iron, Cobalt, and Nickel

Ferrosoferric oxide, Fe_3O_4.—Magnetic oxide of iron occurs free in nature in black octahedral crystals which are magnetic. It is the most stable oxide, and is formed when iron or iron oxides are heated in air or oxygen. According to Moissan, there are two modifications of ferrosoferric oxide: the one is formed by heating ferric oxide from 350° to 400° in a current of hydrogen or carbon monoxide, and the other by reactions at a high temperature, *e.g.* the combustion of iron in oxygen. The former is attacked by nitric acid, and has a specific gravity of 4·86; the latter is not attacked by the same acid, and has a specific gravity 5·0 to 5·1. The phenomenon is thus analogous with the general effect of high temperatures on oxides like alumina, chromic oxide, ferric oxide, etc. Ferrosoferric oxide is not a basic oxide since it forms a mixture of ferric and ferrous salts when treated with acids. It is probably a "compound" oxide, analogous with mangano manganic oxide, Mn_3O_4, and red lead, Pb_3O_4. The relations of the iron oxides thus far considered will appear from the graphic formulæ:

$Fe{=}O$	$O{<}\begin{smallmatrix}Fe=O\\ Fe=O\end{smallmatrix}$	$Fe{<}\begin{smallmatrix}O-Fe=O\\ O-Fe=O\end{smallmatrix}$	$Ca{<}\begin{smallmatrix}O-Fe=O\\ O-Fe=O\end{smallmatrix}$
Ferrous oxide	Ferric oxide	Ferrosoferric oxide	Calcium ferrite

According to this hypothesis, ferrosoferric oxide is a ferrous ferrite, $Fe(FeO_2)_2$. Several other ferrites are known corresponding with the unknown ferrous acid $HFeO_2$. Thus calcium ferrite, $Ca(FeO_2)_2$, that is, $CaO.Fe_2O_3$, is made by precipitating a neutral solution of ferric chloride with lime water. Copper and cobalt ferrates, like ferrous ferrite, are strongly magnetic.

Cobalto-cobaltic oxide, Co_3O_4, is formed in a similar way to ferrosoferric oxide, and it has probably the same constitution. There is some doubt about the existence of the corresponding nickel compound, although it is reported to have been formed when moist oxygen is passed over nickel chloride heated to about 400°.

Peroxides.—Two probably isomeric nickel dioxides have been reported—a black dioxide is made by the action of bromine, or hypochlorites or hypobromites on nickelous hydroxide; and a green one by the action of hydrogen peroxide on nickelous chloride in the cold, followed by treatment with alcoholic potash. The former appears to be a dioxide or polyoxide, and the latter a peroxide or superoxide. If nickel oxide be heated with barium carbonate in an electric furnace, a dark coloured crystalline mass of barium nickelite, $BaO.2NiO_2$, is formed. Barium nickelite is decomposed by water. If cobalt hydroxide be suspended in water, and then treated with hydrogen peroxide, the resulting liquid, after filtration, is strongly acid, and it is supposed to contain cobaltous acid, H_2CoO_3. A green unstable solution of potassium cobaltite, K_2CoO_3, is formed by the addition of potassium hydrogen carbonate, $KHCO_3$, to the solution of cobaltous acid.

Ferric acid and the ferrates.—When chlorine is passed through a strong solution of potassium hydroxide in which ferric hydroxide is suspended, the solution assumes a purple colour, and a black powder of potassium ferrate, K_2FeO_4, separates. This appears to be analogous with potassium manganate, K_2MnO_4. The powder dissolves in water forming a rose red

solution The salt has been prepared in dark-red crystals isomorphous with potassium sulphate and chromate Potassium ferrate is unstable and its solution readily decomposes $4K_2FeO_4 + 10H_2O = 8KOH + 4Fe(OH)_3 + 3O_2$. The barium salt, $BaFeO_4$, is more stable By analogy with the chromates and sulphates, it is inferred that the ferrates are derived from an unknown ferric acid, H_2FeO_4, which in turn is derived from an unknown ferric anhydride, FeO_3, analogous with sulphur and chromic trioxides. $2Fe(OH)_3 + 10KOH + 3Cl_2 = 2K_2FeO_4 + 6KCl + 8H_2O$.

§ 11. Cobalt and Nickel.

History —The word "cobalt" occurs in the writings of B Valentine and Paracelsus to denote a goblin supposed to haunt a mine—from the German *kobald*, an evil spirit The term was also applied to what were called "false ores," that is, ores which did not give metals when treated by the processes then in vogue for the extraction of the metals. The term was gradually confined to the minerals used for colouring glass blue, and which are still used for making smalt. In 1735 Brandt stated that the blue colouring principle is due to the presence of a metal which he called "cobalt rex," hence our "cobalt"

Nickel seems to have been known to the Chinese in early times In Europe, towards the end of the seventeenth century, the German term *kupfer-nickel* (false copper) was applied to an ore, which, while possessing the general appearance of a copper ore, yet gave no copper when treated by the general process then used for the extraction of copper Nevertheless the mineral was supposed to be an ore of copper A F Cronstedt, 1751–1754, stated that kupfer-nickel contains a metal which gives a brown, not a blue colour, with glass Cronstedt's views were not adopted until T Bergman proved clearly that Cronstedt's "nickel" was a new element in an impure condition

Occurrence —Cobalt and nickel are nearly always found associated with one another Both elements occur free in some meteorites Cobalt occurs as a minor constituent in some minerals It also occurs combined as arsenide in *smaltite* or cobalt speiss, $CoAs_2$, and as *cobaltite* or cobalt glance, CoAsS Nickel occurs as *kupfernickel* or *niccolite*, NiAs, *millerite*, or nickel blende, NiS, *nickel glance*, NiAsS, and *garnierite*, a silicate of magnesium and nickel, $(NiMg)H_2SiO_4$, found in New Caledonia

Preparation —The cobalt ores are usually worked to get cobalt salts, and not the metal. The ores are first roasted to remove arsenic and sulphur. The resulting oxides are digested with hydrochloric acid, and the solution treated with hydrogen sulphide to remove the copper, lead, antimony, etc Bleaching powder is then added in just sufficient quantity to oxidize the iron, which is then precipitated by the addition of chalk. The clear solution is treated with more bleaching powder to precipitate the cobalt oxide, any nickel which might be present is precipitated by the addition of milk of lime Cobalt metal is obtained by reducing the oxide in a current of hydrogen, or by reducing the oxide with aluminium powder as in Goldschmidt's process for chromium, Fig 170

Nickel and cobalt ores are treated by different methods depending upon the nature of the ore under treatment Many ores are treated by a process similar to that described for the extraction of copper The ore is "Bessemerized" in a converter, Fig 145, so as to oxidize the iron, and

furnish a matte rich in copper and nickel This is roasted, and the resulting oxides are reduced with coke An alloy of copper and nickel is thus obtained The two metals are separated by an electrolytic process

A nearly pure nickel is made by Mond's process, which is based upon the formation of a readily volatile compound of nickel—nickel carbonyl, $Ni(CO)_4$ The roasted ore (oxides) is heated in a reducing atmosphere to about 300° so as to transform the oxides to metal The resulting mixture is heated with carbon monoxide under a pressure of about 15 atmospheres at a temperature of about 100° The vapours of the escaping nickel carbonyl can be decomposed by heating the gas to 200° under atmospheric pressure The escaping carbon monoxide is used again

Properties.—Cobalt and nickel are hard white metals, cobalt is slightly bluer than nickel Both metals are malleable and ductile. Iron is strongly magnetic, cobalt and nickel are but feebly magnetic, iron forms Fe_3O_4 when heated with steam, nickel and cobalt form the monoxides Iron rusts in moist air, cobalt and nickel only oxidize very slightly unless heated in air Dilute hydrochloric and sulphuric acids dissolve cobalt and nickel slowly, whereas iron is rapidly dissolved by these acids Cobalt and nickel are both attacked by nitric acid, forming the corresponding nitrates—$Co(NO_3)_2$ and $Ni(NO_3)_2$.

Alloys and Uses.—*Nickel is much used for "nickel plating" other* metals on account of its silvery appearance, and the fact that it does not readily tarnish in air The nickel is deposited from a double sulphate of ammonium and nickel by a process similar to that used for "silver and gold plating" Nickel is used in making several important alloys *E g* *German silver* has 25 per cent of nickel and the rest copper and zinc, *nickel steel* is hard and tough, and is used for parts of machinery designed to withstand continuous wear and shocks, and in the manufacture of armour plates, burglar proof safes, etc Nickel coins contain about 25 per cent of nickel, and 75 per cent of copper

Cobalt oxides and silicates are used for colouring glass, and pottery glazes, etc Smalt is a glass made by fusing cobalt oxide and silica, and when ground it is used as a pigment *Thenard's blue* is a blue pigment made by calcining a mixture of cobalt oxide with alumina.

Atomic weights of cobalt and nickel.—The almost identical values for the atomic weights of cobalt and nickel has attracted much attention Nickel oxalate, cyanide, sulphate, chloride, bromide, iodide, etc, have been investigated, and the result shows that the combining weight of nickel (oxygen = 16) lies somewhere between 58 03 and 58 95, and 58 68 is generally accepted as the best representative value Similarly for cobalt the combining weight lies somewhere between 58 7 and 59·7, and 58 97 is generally taken to be the best representative value These numbers agree with the atomic weights estimated from the specific heats by Dulong and Petit's approximation

§ 12 The Relationships of the Members of the Iron Family

The atomic weights of the iron, cobalt, and nickel group are not very different numerically It is not at all uncommon to find that elements with but small differences in their atomic weights show marked differences in their physical and chemical properties For example, boron, 11, and carbon, 12, potassium, 39 1, *argon*, 40, calcium, 40 1, selenium, 79 2;

and bromine, 79 96, iodine, 126 97, tellurium, 127 6 The physical properties of the iron, cobalt, and nickel family are summarized in the table.

TABLE XXXII—PHYSICAL PROPERTIES OF THE IRON FAMILY

	Iron	Cobalt	Nickel
Atomic weight	55 85	58 97	58 7
Specific gravity	7 8	8 5	8 8
Atomic volume	7 16	6 94	6 68
Melting point	1530°	1467°	1435°
Boiling point	2450°	—	2450°

The elements are usually associated together in nature, they are all magnetic, nearly white, hard metals with a high melting point Their chemical properties exhibit a gradual transition from iron to nickel Iron forms two well defined basic oxides, so does cobalt, but the basicity of the cobalt sesquioxide is so feeble that the corresponding salts are only known in solution—the double salts, however, are stable Nickel gives only one basic oxide—nickel monoxide—the sesquioxide does not appear to form salts Although the atomic weight of nickel is less than that of cobalt, the physical and chemical properties of the members of the family show a transition from iron to cobalt to nickel. This is not a common phenomenon with the other family groups It is common to find that in groups of related elements each member seems to affect a particular state of oxidation or combination in which it is in a condition of maximum stability, or chemical repose, as W A Tilden expresses it (1895), and to further emphasize the idea, he points out that the aluminic salts cannot be reduced to a lower state of oxidation, chromic salts can be reduced with difficulty, ferric salts are easily transformed to ferrous salts, while the manganic salts can be reduced by mere heating Ferric chloride is a stable salt, cobaltic chloride is stable only in solution, and nickelic chloride is unknown. A series of polyiodides $MI_2.I_2$ or MI_4 are known—where M stands for an atom of manganese, iron, cobalt, or nickel. The special property of cobalt in forming well-defined ammines is worthy of note The three elements are related to aluminium, manganese, and chromium through iron (ferrates, chromates, manganates, and the alums), and to copper through nickel The isomorphic relationship of the elements iron, cobalt, nickel, aluminium, manganese, and chromium is not only emphasized by the crystalline form of many salts, but also by their constant association in native minerals—*e g* the replacement of aluminium by iron in silicates Nontronite, Fe_2O_3 $2SiO_2$ $2H_2O$, and kaolinite, Al_2O_3 $2SiO_2$ $2H_2O$, for instance, appear to be the terminal members of a series with all intermediate proportions of ferric and aluminium oxide, and there are reasons for supposing chromic oxide can act in a similar way The contrast of chromic iron ore FeO Cr_2O_3 with magnetic oxide of iron, FeO Fe_2O_3, is also of interest To emphasize the relation between copper and nickel, the general colour of their salts, the solubility of the hydroxide in an excess of ammonia to form blue solutions, the isomorphism of their two sulphates *in spite of the fact that their stable* forms are respectively $CuSO_4$ $5H_2O$ and $NiSO_4$ $7H_2O$ respectively The two sulphates form mixed crystals such that if the copper be in excess, both copper and nickel form pentahydrates, and if the nickel be in excess, heptahydrates

Questions

1 State the essential chemical difference between the Bessemer and the open hearth processes for the production of steel What changes are common to both processes? What is the "basic Bessemer process," and why is it of importance?—*Worcester Polytechnic Inst, U S A*

2 Give an account of the metal nickel, and contrast its properties with those of allied elements—*London Univ*

3 Why should the limestone in the Bessemer and the Thomas Gilchrist processes purify steel, when limestone is always present in the previous blast furnace process?—*Amherst Coll, U S A*

4 Write the equation for the action of potassium permanganate on ferrous sulphate and dilute sulphuric acid

5—(*a*) How would you make sodium chromate from chromium sulphate? (*b*) Show how you would change the product above into chromium sulphate and write the equation—*Amherst Coll U S A*

6 How would you make (1) ferrous chloride from iron, (2) ferrous sulphide from ferrous chloride, (3) ferrous sulphate from ferrous sulphide, (4) ferric hydroxide from ferrous sulphate? Write the equations for the reactions after giving the descriptions of the processes and indicate the colour of the product in each case—*Sheffield Scientific School, U S A*

7 Describe briefly and explain the blast furnace process, giving the purpose of each ingredient of the charge—*Amherst Coll, U S A*

8 What is the difference in composition between wrought iron, cast iron, and steel?—*Sheffield Scientific School, U S A*

9 How is ferrous chloride converted into ferric chloride? How is ferric chloride changed to ferrous chloride?—*Sheffield Scientific School, U S A*

10 What is the difference between a blast furnace and a reverberatory furnace, and what is the chief use of each? What is meant by a "flux," and what is one of the most commonly employed substances of this class?—*Princeton Univ, U S A*

11 What is the difference in chemical composition between cast iron, wrought iron, and steel? How and under what conditions do the following substances act upon iron Water, copper, sulphate, sulphuric acid, aqua regia, chlorine?—*London Univ*

12 Describe exactly how you would prepare ferrous sulphate and ferric chloride from metallic iron and also how you would prepare ferrous phosphate from the first, and ferric oxide from the second of these salts, state the appearance of each product—*London Univ*

13 What are the chief sources of nickel? How can nickel be obtained free from cobalt? For what purpose does nickel find employment in the arts? By what properties are nickel compounds distinguished from those of cobalt?—*Board of Educ*

14 What are, most probably, the highest states of oxidation of chlorine, chromium, iodine, and iron? Give an account of the experimental evidence in favour of the views you support—*Board of Educ*

15 What proportion of carbon is necessary in mild steel and hard steel respectively, and what views are now held as to the condition in which carbon exists as steel?—*Board of Educ*

16 Would the following equation represent correctly the formation of potassium ferrate from ferrous hydroxide when the latter is suspended in a solution of potassium hydroxide, and chlorine afterwards passed into the solution $Fe(OH)_2 + 2KOH + 2Cl_2 = K_2FeO_4 + 4HCl$? What objections can be urged against the equation as describing the formation of potassium ferrate in this way?—*R Galloway*

17 What is meant by the statement that the combining weight of hydrogen is 1, that of oxygen 8, and that of iron 28? How are these values arrived at? Why is the combining weight doubled to give the atomic weight of *either* oxygen *or* iron?—*Board of Educ*

18 Describe, with all essential practical details, the preparation of pure specimens of the following salts—(*a*) ferrous sulphate from iron pyrites, (*b*) mercuric chloride from cinnabar, (*c*) barium nitrate from barium chloride—*Board of Educ*

CHAPTER XXVII

The Oxygen Compounds of Nitrogen

§ 1 Sodium and Potassium Nitrates

Potassium and sodium nitrate are two important salts. The former is also called "nitre" and "saltpetre" The word "nitre" is derived from the Arabic *nitrūm* or *natrūm*, thence the Greek words *nitron* or *nátron*, meaning "soda," while saltpetre is a corruption of the Latin *sal petræ*—"salt of the rock" The salt designated by these two terms is very different from rock salt, and from soda Sodium nitrate is often called "soda nitre" or "Chili saltpetre," to distinguish it from "potash nitre" or "saltpetre" proper

Crystallization of the two nitrates —Potassium nitrate forms

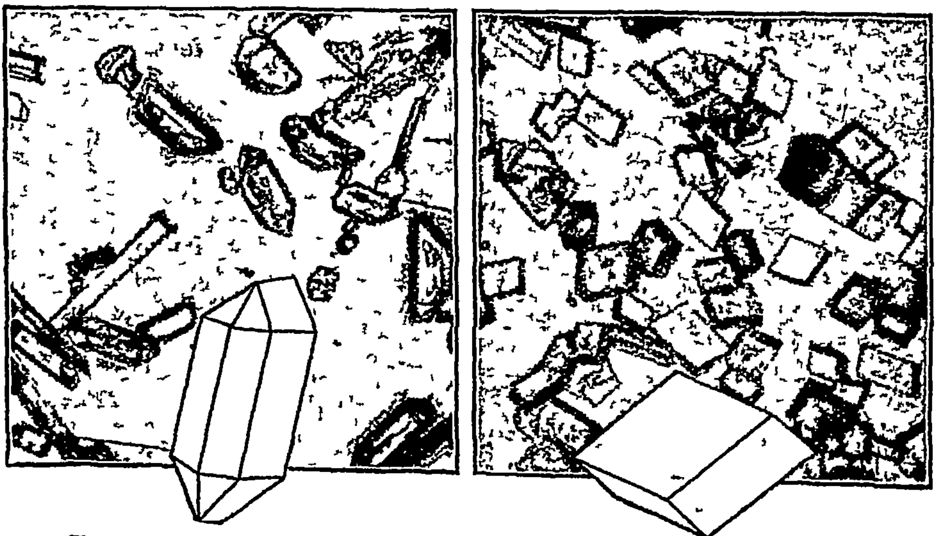


Fig 178 —Potassium Nitrate (left) and Sodium Nitrate (right) Crystals.

hexagonal prisms (rhombic system), and sodium nitrate rhombohedral (trigonal system) crystals The crystals are illustrated in Fig 178, where the salts have been crystallized on a slip of glass and photographed under the microscope Ideal crystals are illustrated by the outline drawings It is really interesting to watch the crystallization of a drop of warm, slightly supersaturated solution of potassium nitrate on a glass

slip under the microscope Crystallization starts at the edges Here rhombohedral crystalline plates (left, Fig 178), which are not really isomorphous with the crystals of sodium nitrate (right, Fig 178), are first formed, although a mixture of the two salts is formed, these are quickly followed by needle like rhombic (trigonal) crystals As a matter of fact, both forms of crystals appear in the photograph (left, Fig 178) Immediately the rhombohedral crystals touch the rhombic crystals, the latter lose their sharp outlines, and needle like rhombohedra sprout forth on all sides (Hence, *potassium nitrate is dimorphous* The rhombic crystals are unstable above, and stable below 129°, and conversely, the rhombohedral crystals are stable above, and unstable below 127° Hence, 129° is a transition temperature

$$\text{Potas nitrate}_{\text{rhombic}} \overset{\leftarrow 129^\circ \rightarrow}{\rightleftharpoons} \text{Potas nitrate}_{\text{rhombohedral}}$$

Both potassium and sodium nitrates are soluble in water, and, although sodium nitrate is more soluble than potassium nitrate at ordinary temperatures, the reverse is true at 100° This is illustrated by the solubility curves—Fig 179—(grams of salt per 100 grams of solvent) from 0° to 100° Sodium nitrate is somewhat deliquescent, that is, it becomes damp on exposure to the air, and it cannot, therefore, be used for some purposes for which potassium nitrate is applicable Potassium nitrate does not deliquesce under the same conditions. Sodium nitrate is much cheaper and more plentiful than the potassium salt.

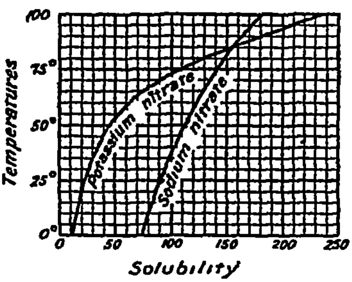


FIG 179 —Solubility Curves of Sodium and Potassium Nitrates

The occurrence of sodium nitrate —Large quantities of sodium nitrate occur in the rainless zone on the West Coast of South America—Peru, Bolivia, Chili The salt occurs in large flat basins between the ridges on the Tarapacca plateau Fig 180 represents a diagrammatic cross section through a "nitre basin" which will give a rough idea how soda nitre occurs There is first a 2 or 3 inch surface layer of grey sand and pebbles. The surface itself is almost devoid of vegetation Below the surface is a 1 to 5 ft layer of similar material cemented together with clay and salt and sodium nitrate This stuff is called by the natives "costra" Below the "costra" is a white stratum of massive nitre bearing rock, 1 to 5 ft thick, which is called by the natives "caliche" Below the caliche is a layer of sodium chloride, etc, resembling costra, a layer of clay and loam, and finally the bed rock of shale, or limestone, or other rock which may be there outcropped Costra is a kind of low grade nitre rock or caliche running 5 to 12 per cent sodium nitrate, the caliche runs 18 to 25 per cent, and in exceptional cases 50 or 60 per cent sodium nitrate—the average runs 20 to 30 per

FIG 180 —Geological Section of Nitre Bed (Diagrammatic)

cent The deposits are close to the surface, and naturally vary a little in different places

The extraction of sodium nitrate —The caliche is mined by boring down to the lowest stratum The bore is enlarged and charged with blasting powder The explosion breaks up the nitre bed within a 50 ft radius of the explosion The caliche is sorted out and transported to the leaching works The caliche is extracted with water, and the solution is recrystallized so as to separate the sodium nitrate from the accompanying impurities—sodium chloride, sodium and calcium sulphates, sodium iodate, sodium perchlorate, insoluble matter, etc Commercial Chili saltpetre contains from 95 to 98 per cent of sodium nitrate The sodium iodate which accumulates in the mother liquid is used for the manufacture of iodine Nearly $2\frac{1}{2}$ million tons of "soda nitre" were exported from Chili in 1911

The conversion of sodium nitrate into potassium nitrate —The Chili saltpetre is dissolved in about $1\frac{1}{2}$ times its weight of boiling water, and a solution of sylvine—potassium chloride, from the Stassfurt deposits —in three times its weight of water, is poured into the sodium nitrate solution Sodium chloride at once separates as a fine granular precipitate $KCl + NaNO_3 \rightleftharpoons NaCl + KNO_3$. The crystals are removed, and the mother liquid is evaporated to about half its original volume, and the sodium chloride again removed. The sodium chloride is washed with water to recover some of the potassium nitrate removed with the crystals, and the washings used for dissolving more of the raw material The mother liquid is further concentrated by evaporation Crude nitre crystallizes from the solution This is purified by recrystallization from boiling water, which is stirred while cooling so that the nitre crystals may be small and granular—" nitre meal " The crystals are dried and packed in sacks for transport The nitre still holds about half per cent of sodium chloride The by-product—pickling salt—is preferred to ordinary salt for pickling meat, probably because of the quantity of nitre it still contains

§ 2 Nitre Plantations

The origin of the nitre beds is not known It is generally agreed that the nitrogen is of organic origin—animal or vegetable Since immense deposits of guano have been found on some of the islands off the coast of Peru—*e g* the Chincha Islands—it has been suggested that the nitrogen is derived from the guano If so, it is not clear where the phosphates have gone, since there is practically no calcium phosphate in the nitre beds Of course, the soluble nitrates may have been leached from decayed guano in some other locality and deposited in their present form But the problem of the origin of the deposits has not been satisfactorily solved

When organic matter decays, say in the soil of cattle yards and stables, ammonia and ammonium compounds are produced by the action of certain bacteria If the soil be fairly dry, but not too dry, a white scum appears on the exposed surface The scum is made up of small crystals of potassium nitrate , and, after a time, if the soil be extracted with water, and strained, the liquid, on evaporation, furnishes yellowish-brown crystals of crude nitre The crude nitre can be purified by re solution and crystallization.

The white efflorescence sometimes seen on the walls of stables, etc, is sometimes, not always, due to the formation of nitrates in this way

The first stage in the decomposition of the organic matter is due to the action of certain bacteria. Ammonia and ammonium compounds are formed along with other gases which produce the characteristic odour of putrefaction. The next stage in the process of decomposition is due to the action of a special bacterium—the nitrous ferment—which converts the ammonia into nitrous acid $2NH_3 + 3O_2 = 2H_2O + 2HNO_2$. Another bacterium—the nitric ferment—transforms the nitrous into nitric acid $2HNO_2 + O_2 = 2HNO_3$. By the agency of these three types of bacteria, the soil is constantly receiving fresh supplies of nitrates necessary for the growth of plants and derived from the decomposition of the organic matter present in the soil [1] The free acids are not really present in the soil because the alkalies or alkaline earths present interact with the acids producing the nitrates and nitrites. It is owing to these reactions that water, contaminated by drainage from surface soil contains nitrates

In the hot dry countries of the East, India, Persia, Arabia, etc, particularly in the neighbourhood of villages where urine and other organic matters find their way into the soil owing to imperfect systems of "sewage disposal." the process of nitrification goes on rapidly The soil is extracted with water every few years, and the nitrates, chiefly calcium and potassium nitrate, are extracted as indicated above The product from the soil in the Valley of the Ganges (Bengal) is called *Bengal saltpetre* it is principally potassium nitrate If calcium nitrate be present, potassium carbonate is added to the aqueous extract from the soil so that calcium carbonate may be precipitated, and potassium nitrate remain in solution $Ca(NO_3)_2 + K_2CO_3 = 2KNO_3 + CaCO_3$. The nitre is then purified by recrystallization.

During the Napoleonic wars, France had great difficulty in procuring sufficient nitre for the manufacture of gunpowder This led to the construction of nitre beds in various parts of the country But when the French ports were thrown open, after these wars, the manufacture of nitre, in France, was abandoned because it could be imported more cheaply from India The process is still used in a few localities—*e.g* Sweden Soil rich in humus, dung, or animal offal is piled into heaps with the *débris* from buildings, or with lime, or wood ashes The heaps are protected from rain by sheds A system of gutters or pipes may also distribute the liquid excretions of animals over the top of the heap The piled mass is called a nitre plantation Before long a white film of nitre "grows" on the windward face of the pile This is scraped off regularly, and leached as indicated above If lime be present, the resulting calcium nitrate is converted into potassium nitrate by the addition of wood ashes—potassium carbonate

§ 3 The Nitrogen Cycle.

All living matter, and the waste products of animals contain considerable quantities of combined nitrogen It is a necessary constituent for the growth of living organisms During the decay of organic matter

[1] Of course, as indicated shortly nitrates occur in rain-water derived from the direct oxidation of nitrogen by electric discharges—lightning, etc.

through the agency of bacteria, part of the nitrogen finds its way back to the atmosphere, and part passes directly into the soil to be absorbed by plants. Animals cannot assimilate free nitrogen, and they are accordingly dependent upon the plants for their supply. Nor can plants usually obtain their nitrogen direct from the atmosphere. Most plants get their nitrogen from the soil where it is present in the form of nitrates, ammonium, or other complex compounds. The organic matter in the soil is attacked by bacteria of various kinds, and part is converted into nitrates and part into free nitrogen. A certain amount is brought back from the atmosphere, during a rain storm, where it has been oxidized into ammonium nitrate by electric discharges. But these supplies of available nitrogen do not suffice to maintain the fertility of cultivated soils. It is therefore necessary to make good the constant draining of the available nitrogen by the cultivated plants. This is done by allowing nitrogenous organic matter—manures—to decay on the soil, or to add a mixture—fertilizer—containing available nitrogen.

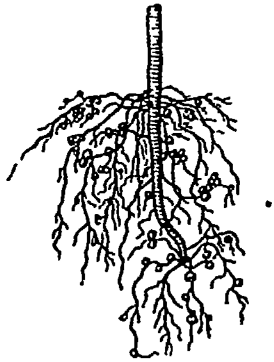
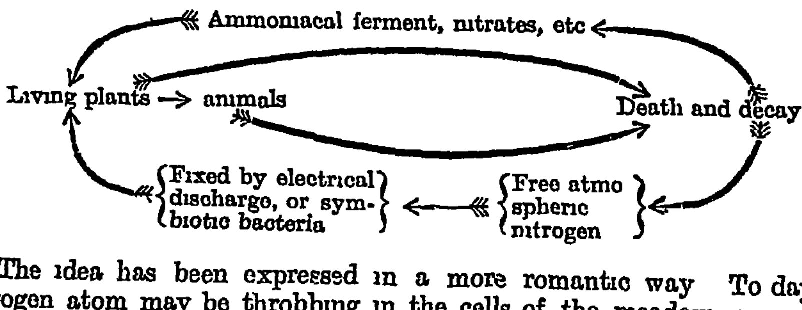


FIG. 181.—Nodules on Root of Bean Plant.

Some plants, principally the leguminosæ—peas, beans, clover, lupins, etc.—appear to live in a kind of partnership—symbiosis (from the Greek συν (syn), with; βίωσις (biosis), living)—with certain bacteria. The bacteria appear to live as guests in nodules on the rootlets of their host, and probably also in the neighbouring soil. The nodules on the rootlets of a *Phaseolus* (bean) are illustrated in Fig. 181.[1] The symbiotic bacteria convert the nitrogen of the atmosphere into a form available as food for the plant on which they live.

The processes involved in the circulation of nitrogen in nature may be summarized in the scheme:



The idea has been expressed in a more romantic way. To-day a nitrogen atom may be throbbing in the cells of the meadow grass; to-morrow it may be pulsating through the tissues of a living animal. The nitrogen atom afterwards may rise from decaying animal refuse, and stream to the upper regions of the atmosphere where it may be yoked with oxygen in a flash of lightning and return as plant food to the soil in a torrent of rain; or it may be directly absorbed from the atmosphere by the soil, and there rendered available for plant food by the action of symbiotic bacteria. Thus each nitrogen atom has doubtless undergone a never ceasing cycle of changes through countless æons of time.

[1] Obtained from Mr. A. Flatters, Manchester.

§ 4 The Fixation of Atmospheric Nitrogen

The fertility of cultivated fields and gardens is dependent upon the amount of combined nitrogen added as manure or fertilizer Of course, cultivated plants require fertilizers containing other elements—particularly phosphorus, and potassium—but nitrogen is the most expensive The development of agriculture is largely dependent upon the cheap production of available nitrogen According to a Report of a Commission for the Chilian Government in 1909, their nitre beds contained at least 250 million tons of caliche, containing over 15 per cent of nitre, yet the consumption is so great that it was predicted the beds would be exhausted in less than a century Most of the sodium nitrate is employed as a fertilizer for wheat, etc Since the comparatively small store available promises soon to be deplenished, it is obviously necessary to exploit other means of supplying farmers with the fertilizers they require The nitre plantations do not give a large enough yield F Nobbe and L. Hiltner, in 1896, sold cultures of the "nitrogen fixing" bacteria under the name "nitragen" for inoculating the soil. The results have been fairly satisfactory for certain crops when peptones and glucose were added to the water in which the nitrifying bacteria are distributed for spreading on the soil

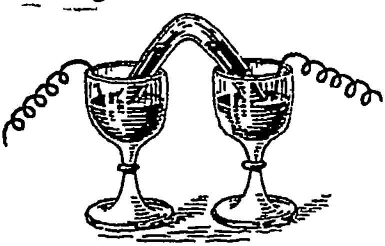


FIG 182 —Cavendish's Experiment

There are at present three promising methods for the conversion, or "fixation" of atmospheric nitrogen in a form available for plant food (1) By heating calcium carbide in dry nitrogen whereby it is converted into calcium cyanamide (*q v*), (2) the direct synthesis of ammonia from its elements (*q v*), and (3) the direct oxidation of atmospheric nitrogen and absorption of the resulting oxides in water or alkaline solutions

J Priestley (1779) first noticed that an acid is formed when electric sparks are sent through the air, but he seems to have thought that the acidity was due to carbonic acid H. Cavendish (1785) proved that the product of the action is nitric acid In Cavendish's experiment, the air was confined over mercury in the bend of a Λ shaped tube The open ends of the tube dipped under mercury contained in separate glasses (Fig 182) A series of sparks was sent from an electrical machine through the air confined in the tube After the action, the gas turned blue litmus red, gave a turbidity with lime water, was absorbed by potassium hydroxide, etc In fine the product of the action of potassium hydroxide upon the air after sparking, was nitre W Crookes (1892) showed that air can be burned to nitric and nitrous acids in a powerful electric arc, and Siemens and Halske (1902) burnt the nitrogen by passing air through a chamber containing an electric arc spread over as great a surface as possible by means of an electro magnet Their apparatus is shown diagrammatically in Fig 183 The conditions of the reaction have been studied by W Nernst (1906), and F Haber (1907) Nitric oxide is formed by the

direct union of nitrogen and oxygen at high temperatures $N_2 + O_2 = 2NO$ The reaction is endothermal The higher the temperature, the greater the amount of nitric oxide formed when the system is in equilibrium Thus, with a mixture of equal volumes of nitrogen and oxygen

Temperature	1811°	2033°	2195°	3000°	3200°
Nitric oxide	0 37	0 64	0 997	4 5	5 00 per cent

The reaction is very rapid A few seconds suffice for the system to assume equilibrium Hence if the reaction is not to be reversed, owing to the dissociation of nitric oxide, the system, after heating, must be cooled very rapidly, as was the case with hydrogen peroxide and ozone Experiment shows that the cooling of the gases to about 700° suffices to make the back action (dissociation of nitric oxide) negligibly small

There are several successful schemes for applying these facts commercially to the fixation of atmospheric nitrogen Birkeland and Eyde's may be taken as typical It is used in Norway Other schemes are in use in the United States, Italy, etc K. Birkeland and S Eyde (1905) produce a high voltage arc between two electrodes consisting of copper tubes through which a current of cold water is continually flowing In order to spread the flame over as great an area as possible, an electromagnet is placed at right angles to the electrodes so that the terminals lie between the poles of the magnet

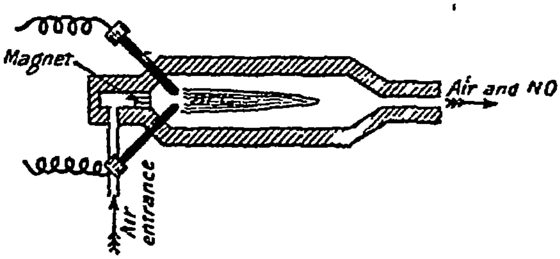


FIG 183 —Siemens and Halske's Experiment

The effect of the magnet is to spread the flame on one electrode until the current is reversed, a new flame then starts on the opposite electrode The current alternates every $\frac{1}{50}$ second, and the general result is an intensely hot disc of flame—"electric sun"—6 feet in diameter The flame is enclosed in a special brick-lined furnace with a metal casing, and air is driven past both sides of the disc of flame The gases are pumped off The "disc arc" (1) offers a very large surface of contact to the air This means that a relatively large percentage of the nitrogen will be oxidized to nitric oxide with a minimum consumption of current, and (2) it allows the system to be cooled rapidly so as to reduce the amount of nitric oxide dissociated during the cooling The gases containing between 1 and 1½ per cent of nitric oxide, at a temperature of about 200°, enter the oxidation chamber where the nitric oxide combines directly with oxygen to form nitrogen peroxide, $2NO + O_2 = 2NO_2$ The gases are then passed through a series of five absorption towers where they meet water, and milk of lime The absorbed nitrogen oxides form calcium nitrate, the solution is evaporated, and sold as fertilizer This *Norwegian saltpetre* is almost anhydrous calcium nitrate It contains nearly 13 per cent of available nitrogen In illustration of the growth of this industry, 115 tons were produced in Norway in 1905, and 9422 tons valued at £72,590 were produced in 1909

§ 5 Nitric Acid—Preparation

Molecular weight, $HNO_3 = 63.02$ Melting point, $-47°$, boiling point, 86° at 760 mm pressure Specific gravity at 0°, 1.56

History—Nitric acid was probably known to the ancient Egyptians Geber says that he made it by distilling copperas with saltpetre and alum, and J R Glauber (1650) made it by distilling a mixture of nitre and sulphuric acid. A. L Lavoisier (1776) proved that nitric acid is a compound of oxygen, and H. Cavendish (1784–85) demonstrated that it is formed by sparking nitrogen with moist oxygen J L. Gay-Lussac (1816) found the ratio of hydrogen oxygen nitrogen corresponded with H_2O N_2O_5

Preparation of nitric acid—When potassium or sodium nitrate is mixed with dilute sulphuric acid, no obtrusive sign of chemical action occurs, although it can be proved that a reversible change has taken place so that the sodium is distributed between the sulphuric and nitric acids. If a mixture of concentrated sulphuric acid and sodium nitrate be heated to about 130°, nitric acid, HNO_3, is volatilized. The reaction is represented

$$NaNO_3 + H_2SO_4 \rightleftharpoons NaHSO_4 + HNO_3$$

The two salts sodium nitrate and sodium hydrogen sulphate are not volatile, the nitric acid, HNO_3, boils at 86°, and the sulphuric acid at 330° Hence on warming to about 100°, the nitric acid is volatilized and the state of equilibrium of the solution is disturbed, in consequence, the sodium nitrate is all decomposed If the temperature be higher, normal sodium sulphate is formed and less sulphuric acid is needed for a given yield of nitric acid $2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3$ But appreciable quantities of the nitric acid are decomposed at the higher temperature

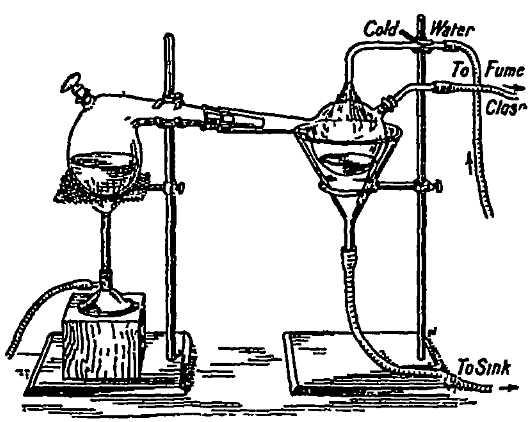


FIG 184.—Preparation of Nitric Acid

The acid can be prepared in the laboratory by means of the apparatus illustrated in Fig 184. This explains itself All rubber and cork stoppers and connections must be avoided because the acid rapidly attacks organic matter The retort is charged with the sodium nitrate and sulphuric acid, and heated. Brownish red fumes appear and the distillate is more or less coloured brown because of the solution of the red coloured gas in the distillate The brownish red gas is a product of the decomposition of the nitric acid by heat. On a manufacturing scale, the sodium nitrate and sulphuric acid are heated in cast iron retorts, the vapour is condensed in earthenware pipes cooled by water, and collected in earthenware jars. The last jar is connected with a tower filled with coke down which a stream

of water trickles The object is to recover the nitrogen peroxide produced by the decomposition of the nitric acid The retort has an exit pipe from which the sodium sulphate can be run when the action is over. To reduce the amount of nitrogen peroxide formed during the decomposition of the nitric acid by heat, the stills are often worked under a reduced pressure so that the acid may come off at as low a temperature as possible

Purification of nitric acid —The nitric acid so obtained contains some chlorine and iodine derived from the chlorides and iodides associated with the nitre Some sodium sulphate, sulphuric acid, and iron are also carried over into the receiver Nitrogen peroxide is also present as indicated above To purify the acid, it is distilled in glass retorts, and the first fraction which come over is put on one side as crude acid containing volatile chlorine compounds. When the distillate gives no precipitate with a dilute solution of silver nitrate, the receiver is changed, and the greater part of the nitric acid is distilled off The residue in the retort contains the sulphates, iodine and iron

The acid can be redistilled from concentrated sulphuric acid to remove all the water, and the nitrogen peroxide can be removed by passing a current of carbon dioxide through the warm acid until it is colourless

Fuming nitric acid is brown in colour, it is nitric acid with a considerable amount of nitrogen peroxide in solution It can be made by distilling nitric acid with a little starch The starch reduces some of the nitric acid to nitrogen peroxide which is absorbed by the distillate

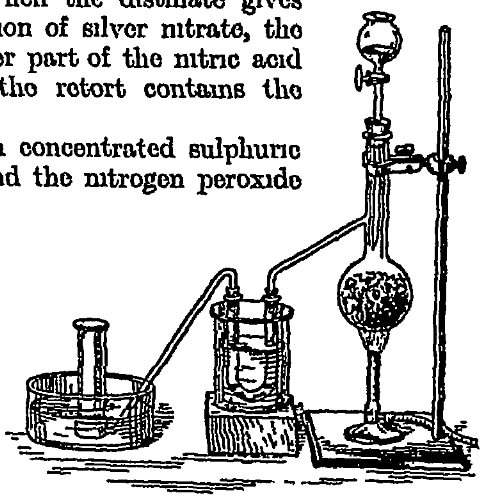


FIG 185 —Decomposition of Nitric Acid by Heat

Uses —Nitric acid is one of the common acids It is used as a solvent for metals, for etching designs upon copper, for the manufacture of nitrates used for photography [$AgNO_3$], pyrotechny [$Ba(NO_3)_2$, $Sr(NO_3)_2$, etc], calico printing [$Pb(NO_3)_2$], etc It is also used in the manufacture of dyestuffs, explosives, sulphuric acid, etc, and in metallurgy, etc A carboy of the acid (sp gr 1 42) holds about 140 lbs The commercial acid sells at about 3¾*d* per lb, and the pure at 4¾*d* per lb

§ 6 The Properties of Nitric Acid

Nitric acid is a colourless mobile liquid which *fumes strongly* in air It has a peculiar smell The pure acid is hygroscopic and rapidly absorbs moisture from the air It mixes in all proportions with water, and, as in the case of sulphuric acid nitric acid contracts when mixed with water, and the mixture rises in temperature The greatest contraction is said to correspond with a mixture of acid and water in the molecular proportions $3H_2O + HNO_3$ The pure acid boils at 86°, and freezes to a white solid, melting at $-47°$ *An aqueous solution* containing 68 per cent. of nitric acid boils at 120 5°, more concentrated solutions, and also more

dilute solutions, boil at lower temperatures A more dilute solution loses water on boiling, and a more concentrated solution loses acid on boiling until 68 per cent. of nitric acid of constant boiling point distils unchanged This is the concentrated nitric acid of commerce The specific gravity of the constant boiling acid at 15° is 1 414.

Decomposition of nitric acid—A certain amount of acid is decomposed during the distillation $4HNO_3 = 4NO_2 + 2H_2O + O_2$. This decomposition commences below 68° At higher temperatures the decomposition is very marked. For instance, if the concentrated acid be allowed to fall drop by drop into a quartz flask containing fragments of calcined pumice stone heated in an apparatus fitted as shown in Fig 185, the red vapours evolved can be condensed in a freezing mixture to a brownish liquid (NO_2), and a colourless gas—oxygen—collects in the gas jar Nitric acid vapour also decomposes when exposed to the light, nitrogen peroxide is formed which is absorbed by the acid giving it a yellow colour

Hydrates of nitric acid—F W Küster and R Kremann's (1904) freezing curve for mixtures of nitric acid and water, Fig 186, shows the existence of two hydrates $HNO_3.3H_2O$ and $HNO_3.H_2O$, see p 437 The first-named hydrate separates in transparent crystals, melting at −18 2°, and the latter in opaque crystals melting at −38° Another hydrate, $HNO_3.2H_2O$, is reported, but it does not appear to be stable under the conditions of this experiment

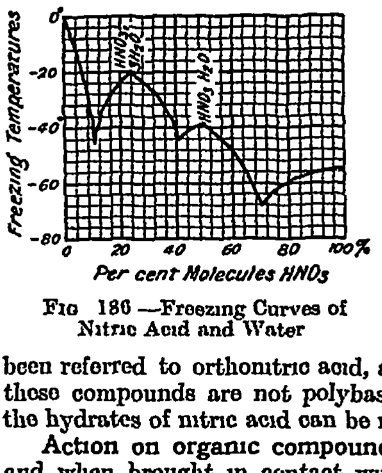


FIG 186 —Freezing Curves of Nitric Acid and Water

With the notation employed in discussing the periodic acids, the acid $N(OH)_5$, should be called orthonitric acid, $NO(OH)_3$, mesonitric acid, and $NO_2(OH)$, metanitric acid The last alone is known with any degree of probability The hydrate $HNO_3.2H_2O$ has been referred to orthonitric acid, and $HNO_3.H_2O$ to mesonitric acid, but these compounds are not polybasic acids, and it is therefore doubtful if the hydrates of nitric acid can be interpreted in this way

Action on organic compounds—Nitric acid is extremely corrosive, and when brought in contact with the skin causes painful sores The dilute acid stains the skin yellow or brown, probably owing to the formation of xanthoproteic acid. If strong nitric acid be poured on sawdust, the mass often bursts into flame If a dish of fuming nitric acid be placed in a basin in the bottom of a glass cylinder, and a little turpentine be added from a pipette, the turpentine will burst into flame Glowing charcoal continues to burn when plunged into the acid With organic compounds, one or more hydrogen atoms are replaced by an equivalent NO_2 radicle, and water is formed. For instance, cellulose or cotton $C_{12}H_{20}O_{10}$, becomes nitrocellulose or gun cotton, $C_{12}H_{14}O_{10}(NO_2)_6$, glycerol, $C_3H_5(OH)_3$, becomes nitroglycerol, $C_3H_5(ONO_2)_3$, which is the active agent in dynamite, and phenol, C_6H_5OH, becomes picric acid, $C_6H_2(OH)(NO_2)_3$, which is the active agent in melinite

Oxidizing action of nitric acid—In consequence of the great proportion of oxygen in nitric acid, and in consequence of the ease with which it

is decomposed, we should expect nitric acid to be a strong oxidizing agent. It is so. Sulphur is oxidized to sulphuric acid, *e.g.* $S + 2HNO_3 = H_2SO_4 + 2NO$; and also phosphorus to phosphoric acid, iodine to iodic acid, arsenious oxide to arsenic oxide, antimony to antimonic oxide, ferrous to ferric salts, etc. Many metallic sulphides—iron, lead, etc.—are oxidized by nitric acid to sulphates: $2FeS_2 + 10HNO_3 = Fe_2(SO_4)_3 + H_2SO_4 + 10NO + 4H_2O$.

Aqua regia.—A mixture of hydrochloric and nitric acids—say, in the proportions 3 or 4 volumes of the former per one volume of the latter—will dissolve the metals gold and platinum. Hence the alchemists term for this mixture, *aqua regia*—the kingly water—because it dissolves the very king of metals, gold. The mixture becomes coloured at about 10°, and it evolves gas at about 30°; the action is quite vigorous about 90°, and at 109° a mixture of nitric and hydrochloric acids distils over. The action of *aqua regia* on gold is supposed to be due to the oxidation of the hydrochloric acid by the nitric acid whereby chlorine is formed, and this latter agent attacks the gold or platinum. Goldschmidt's equation is $HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2$, corresponding with the fact that some nitrosyl chloride—NOCl—is formed at the same time. The greater oxidizing properties of aqua regia over nitric acid are generally attributed to the presence of the free chlorine. The action on metallic sulphides, MS, is represented: $3MS + 6HCl + 2HNO_3 = 4H_2O + 2NO + 3MCl_2 + 3S$. This equation is imperfect since there is no doubt that the reaction is much more complex.

Action on the metals.—The purest acid does not attack carbonates, nor does it dissolve mercury, copper, silver, cadmium, but sodium takes fire in the acid. Most metals and the carbonates are vigorously attacked by ordinary nitric acid, and for this reason the old alchemists called it *aqua fortis*—the strong water; or *aqua dissolutiva*—the dissolving water. The acid does *not attack the so called noble metals, gold, platinum, rhodium, and iridium.* Tin with the dilute acid gives tin nitrate, $Sn(NO_3)_2$; but with the concentrated acid it forms nitrogen peroxide, NO_2, and probably $Sn(NO_3)_4$, which is immediately decomposed by the heat of the reaction, so that stannic oxide, SnO_2, appears as the product of the action: $Sn(NO_3)_4 = SnO_2 + 4NO_2 + O_2$. With mercury, an excess of the acid produces mercuric nitrate, $Hg(NO_3)_2$; and with an excess of mercury, mercurous nitrate, $HgNO_3$. For the action of nitric acid on iron, and nickel, see "Passive state." The action of aqua regia (*q.v.*) is more vigorous than nitric acid alone.

The action of nitric acid on the metals generally, is somewhat complex, because the main reaction is complicated by side or concurrent, and by consecutive reactions. These again depend not only upon the particular metal under consideration, but also on the concentration of the acid, the temperature, and the concentration of the products of the reaction accumulating in the solution. For instance, when dilute nitric acid acts upon copper, copper nitrate and a colourless gas, nitric oxide, are formed: $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$; but as the copper nitrate accumulates in the solution, nitrous oxide and even nitrogen may be found in appreciable quantity among the products of the reaction; again, with concentrated nitric acid, nitrogen peroxide is the main gaseous product of the reaction: $Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2$. Similarly with zinc, dilute nitric acid forms nitrous oxide: $4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 5H_2O + N_2O$; but with a more concentrated acid, ammonia

may be formed $4Zn + 9HNO_3 = 4Zn(NO_3)_2 + 3H_2O + NH_3$ The ammonia, of course, reacts with some of the nitric acid to form ammonium nitrate. Iron filings or a copper zinc couple in the presence of a little sulphuric acid reduces dilute nitric acid to ammonia

The mechanism of the reaction —Some consider that the first product of the reaction is a nitrate of the metal and nascent hydrogen $Cu + 2HNO_3 = Cu(NO_3)_2 + [2H]$. The nascent hydrogen is then supposed to reduce the nitric acid to nitrous acid. With some metals, the reduction of the nitric acid proceeds much further, say through the stages $NO_2 \rightarrow HNO_2 \rightarrow NO \rightarrow N_2O \rightarrow N_2 \rightarrow NH_3$ Free hydrogen is seldom evolved because it is so rapidly oxidized by the nitric acid. However, free hydrogen is said to have been obtained by the action of nitric acid on manganese, and on magnesium The reducing actions indicated above can be represented symbolically

$$2HNO_3 + [2H] = 2H_2O + 2NO_2, \quad 2HNO_3 + [8H] = 5H_2O + N_2O$$
$$2HNO_3 + [4H] = 2H_2O + 2HNO_2, \quad 2HNO_3 + [10H] = 6H_2O + N_2$$
$$2HNO_3 + [6H] = 4H_2O + 2NO, \quad 2HNO_3 + [16H] = 6H_2O + 2NH_3$$

Some believe that the acid first oxidizes the metal to the oxide, *e.g* $3Cu + 2HNO_3 = 3CuO + H_2O + 2NO$, and that the oxide then dissolves in the acid to form the nitrate $CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O$ *When differences of opinion can reasonably be entertained, it follows that our knowledge of the facts is incomplete, and more experimental work is needed* The metals copper, silver, mercury, and bismuth, have no perceptible action on cold dilute sulphuric and hydrochloric acids, and accordingly it is not likely that they will reduce nitric acid by the action of nascent hydrogen V H. Veley (1890) proved that these metals have no action on cold dilute nitric acid unless a trace of nitrous acid or a lower nitrogen oxide is present. Nitrous acid may be present in the nitric acid as an impurity, it may be formed by the incipient decomposition of nitric acid when it is warmed, or it may be formed in the acid by electrolysis produced by local currents of electricity set up by impurities in the metal ("local action") Once the action has started, the evolution of nitric oxide, and the formation of nitrate proceed quickly According to Veley, therefore, the dissolution of this metal in nitric acid proceeds $Cu + 3HNO_3 = Cu(NO_3)_2 + HNO_2 + H_2O$, is the resultant of a series of consecutive reactions $Cu + 4HNO_2 = Cu(NO_2)_2 + 2H_2O + 2NO$, followed by $Cu(NO_2)_2 + 2HNO_3 = Cu(NO_3)_2 + 2HNO_2$, the small trace of nitrous acid thus acts as a catalytic agent, nitrous acid is continuously produced, and continuously decomposed $3HNO_2 = HNO_3 + 2NO + H_2O$

Nitric anhydride, nitrogen pentoxide —Add phosphorus pentoxide to well cooled pure nitric acid in a retort. Heat the retort, at as low a temperature as possible so that a deep orange coloured distillate is obtained. The distillate separates into two layers. Decant the upper layer[1] into a stoppered test-tube, when this liquid is cooled in ice cold water, crystals separate Pour off the orange liquid from the crystals. Melt the crystals at as low a temperature as possible, and again cool the liquid Pour off the mother liquid By repeating this operation, white rhombic crystals or six sided prisms melting at 30°, and boiling at 47°, are obtained The

[1] The lower layer is a solution of nitrogen pentoxide in nitric acid This is liable to explode when heated.

phosphorus pentoxide has removed the elements of water from the nitric acid $P_2O_5 + 2HNO_3 = 2HPO_3 + N_2O_5$ This substance is also made by the action of dry chlorine on silver nitrate in a U-tube between 60° and 95° The nitrogen pentoxide reacts with water producing nitric acid $N_2O_5 + H_2O = 2HNO_3$ Hence the crystalline mass is to be regarded as nitric anhydride.

H St C Deville (1849) analyzed this compound by passing the vapour over hot copper The copper retained the oxygen, and the nitrogen passed on $N_2O_5 + 5Cu = 5CuO + N_2$ The results of the analysis correspond with nitrogen 25 65 per cent, oxygen 74 35 per cent, that is, with the formula $(N_2O_5)_n$ The molecular weight has not been determined Hence we take the simplest—N_2O_5 The structure of nitric acid is nearly always represented by

$$\mathrm{HO-N}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{O}\end{smallmatrix}$$

corresponding with quinquevalent nitrogen This agrees with the ready decomposition of the pentoxide into nitrogen peroxide, NO_2, and oxygen The formula of the pentoxide is best represented as indicated above

There is a little, but no satisfactory, evidence that the molecule of liquid nitric acid is $(HNO_3)_2$, or $H_2N_2O_6$ The density of the vapour of nitric acid at 86° is 59 2 ($H_2 = 2$), and at 256°, 36·0 The former is supposed to correspond with a 9 5 per cent dissociation of the vapour HNO_3, and the latter with a 100 per cent dissociation $4HNO_3 \rightleftharpoons 4NO_2 + 2H_2O + O_2$

§ 7 Hyponitrous Acid and the Hyponitrites

Reduction of nitrites and nitrates—The reduction of nitrites and nitrates to ammonia readily occurs in alkaline solutions For example, if an excess of sodium or potassium hydroxide be added to nitric acid, and pure zinc, aluminium, or iron be added to the alkaline solution, the salt is reduced to ammonia When a solution of potassium or sodium nitrite or nitrate is treated with a solution of metallic sodium in mercury—sodium amalgam—the hydrogen liberated reduces the nitrite or nitrate, forming a new salt—sodium hyponitrite $2NaNO_3 + [8H$ $= 4H_2O + Na_2N_2O_2$ The alkaline solution can then be neutralized by acetic acid, and when silver nitrate is added, a yellow precipitate of silver hyponitrite, $Ag_2N_2O_2$, is formed By treating silver hyponitrite with a solution of hydrogen chloride in dry ether, and evaporating the clear solution, white deliquescent crystalline plates are obtained This is *hyponitrous acid* The solid is very unstable and is liable to explode even below 0° The aqueous solution soon decomposes into water and nitrous oxide $H_2N_2O_2 = H_2O + N_2O$ The same substance, hyponitrous acid, is produced when hydroxylamine acts upon nitrous acid. $NH_2OH + HNO_2 = H_2N_2O_2 + H_2O$

Constitution—Hyponitrous acid is dibasic, and the formula $H_2N_2O_2$ has been established by freezing-point methods Its constitution is best represented by $HO-N=N-OH$ It is conceivable that the molecule may have two different structures represented graphically by

$$\begin{array}{c} \mathrm{N-OH} \\ \| \\ \mathrm{HO-N} \end{array} \quad \rightleftharpoons \quad \begin{array}{l} \mathrm{N-OH} \\ \| \\ \mathrm{N-OH} \end{array}$$

This means that with our present system of representing the composition of compounds, the hydroxyl groups may be disposed either on the same side of the molecule—the syn type, or on opposite sides of the molecule—the anti type Evidence of the existence of both forms has been obtained in organic chemistry It will be observed that this form of isomerism may or may not exhibit a phenomenon resembling desmotropism, or tautomerism

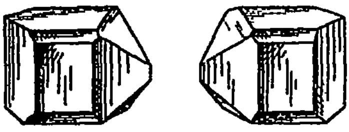


FIG 187 —Crystals of Dextro and Lævo tartaric Acids

A striking example of this phenomenon was discovered by L. Pasteur in 1860 Tartaric acid—

$$COOH.CH(OH).CH(OH).COOH$$

—exists in three forms, all have the same molecular weight, and the only apparent difference in their properties is connected with their behaviour towards polarized light The most satisfactory method of representing the constitution of the three tartaric acids in harmony with the facts, and with the atomic hypothesis, is as follows

TRANS FORMS		CIS FORM
COOH HO—C—H H—C—OH COOH	COOH H—C—OH HO—C—H COOH	COOH H—C—OH H—C—OH COOH
Dextro tartaric Acid	Lævo tartaric Acid	Inactive Tartaric Acid

There is one cis structure, and two modifications of the trans structure—the dextro and lævo acids The cis structure is inactive towards polarized light, while one of the trans forms deflects the ray of polarized light to the right (dextro tartaric acid), and the other to the left (lævo tartaric acid) There is no difference in the kind or number of atoms or radicles in the molecules of the different varieties. Crystals of the dextro and lævo acids or their salts are similar, but enantiomorphic—from the Greek ἐναντιος (enantios), opposite, μορφή (morphe), shape—meaning that the two crystals are related to one another as object and image, or as right and left-handed screws—Fig 187 It is therefore inferred that the radicles in the two varieties are so disposed that the molecules of the two varieties rotate or spin in opposite directions, and that the third inactive variety (mesotartaric acid) is a kind of hybrid of the other two in that the tendencies to rotate in opposite directions neutralize one another This is illustrated by the arrows in the above structural formulæ

Instead of representing the disposition of the radicles in the molecules on a plane surface, it is maintained that the structural formulæ ought to be represented in three dimensions, as is usually done in organic chemistry, where this subject has been highly specialized Hence the terms stereoisomerism—from the Greek στερεός (stereos), solid—or geometrical or physical isomerism Many of the concepts which have been developed

in organic chemistry have been extended into inorganic chemistry. The "syn" and "anti" forms of hyponitrous acid are simple examples. Sometimes the carbon atom behaves as if its valency linkages were directed from the centre towards the four apices of a regular tetrahedron. The real shape of the atom of carbon is, of course, unknown. Similar attempts have been made to deal with the atom of nitrogen and some other elements, but in these cases there is not the same agreement among chemists as is the case with carbon. See "Werner's theory of valency."

§ 8 Nitrates

Nitric acid is a strong acid, it colours blue litmus red, and behaves as a monobasic acid with metallic oxides, hydroxides, and carbonates forming a series of salts called nitrates. For instance, with copper oxide copper nitrate is formed: $CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O$, etc. Similarly we have potassium nitrate, KNO_3, calcium nitrate, $Ca(NO_3)_2$, bismuth nitrate, $Bi(NO_3)_3$, etc.

The nitrates are usually readily soluble in water and form well defined crystals. The nitrates are decomposed when heated. Lead nitrate, and the nitrates of the heavy metals generally form an oxide of the metal and give off a mixture of oxygen and nitrogen oxides: $2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$; $2Pb(NO_3)_2 = 2PbO + O_2 + 4NO_2$. The nitrates of the alkalies form nitrites and oxygen: $2KNO_3 = 2KNO_2 + O_2$. Hence the nitrates are often used as oxidizing agents.

Silver nitrate, $AgNO_3$.—Silver nitrate is usually formed by the action of nitric acid on the metal. The aqueous solution crystallizes in colourless rhombic plates, 100 grams of water at 0°, dissolve 122 grams of the salt; at 50°, 455 grams; and at 100°, 952 grams of the salt. The aqueous solution is blackened, probably by reduction to silver, by contact with organic matter, and it is accordingly used as marking ink for linen, etc. The crystals melt at 209°, and solidify to a fibrous crystalline mass called "lunar caustic." The salt decomposes at 450°, forming silver nitrite, $AgNO_2$, and, at higher temperatures decomposes into metallic silver and nitrogen oxides. Silver nitrate absorbs ammonia gas with some avidity, forming $AgNO_3.3NH_3$; the aqueous solution when saturated with ammonia deposits rhombic prisms of $AgNO_3.2NH_3$.

Composition and basicity of nitric acid.—To show how the basicity and composition of the acid can be determined. One gram of pure silver was dissolved in an excess of nitric acid, and on evaporation to dryness, a weight 1.5748 gram of silver nitrate was obtained. This silver nitrate was heated in a current of carbon dioxide, and the vapours passed over hot metallic copper. The copper retained the oxygen. The gases were collected over a solution of potassium hydroxide which retained the carbon dioxide, not the nitrogen. The volume of nitrogen collected corresponded with 0.1307 gram. Assuming that the atomic weight of silver is 107.88; oxygen, 16; it follows that

	Grams
Weight of silver nitrate	1.5748
Weight of metallic silver	1.0000
Weight of "nitrate" radicle	0.5748
Weight of nitrogen	0.1307
Weight of oxygen	0.4441

Hence in silver nitrate, the N : O = 0.1307 : 0.4441 by weight, i.e. the numbers of the atoms are related as N : O = 0.0093 : 0.028, or, as 1 : 3. Hence for every atom of silver, there are three atoms of oxygen and one atom of nitrogen—$AgNO_3$. Assuming this composition for silver nitrate, it follows that the combining weight of nitrogen can be determined directly from the data given. No one has prepared two silver nitrates—acid and normal silver nitrates—and there is no evidence of dibasicity with nitric acid. Hence it is inferred that nitric acid is monobasic.

Copper nitrate, $Cu(NO_3)_2.3H_2O$.—An aqueous solution of copper nitrate is obtained by the typical methods for the preparation of salts—the action of nitric acid on the metal, oxide, hydroxide, or carbonate. The solution deposits deliquescent crystals of $Cu(NO_3)_2.3H_2O$, and when heated to about 60°, the crystals decompose, forming basic copper nitrate, $Cu(NO_3)_2.3Cu(OH)_2$. Anhydrous copper nitrate, $Cu(NO_3)_2$, has not been made.

Mercurous nitrate, $HgNO_3$, is deposited in colourless monoclinic crystals of $HgNO_3.H_2O$ from solutions of mercury in cold dilute nitric acid (mercury in excess). The salt dissolves in water acidulated with nitric acid, but an excess of water decomposes the salt with the precipitation of a basic nitrate, $HgOH.HgNO_3$. If this be boiled with water, it is converted into mercuric nitrate and mercury; if an excess of mercury be also present, the basic mercurous nitrate $3HgNO_3.2HgOH$ is formed. Mercuric nitrate, $Hg(NO_3)_2$, is prepared by boiling mercury with an excess of nitric acid until the solution gives no precipitate with a little sodium chloride. If evaporated over sulphuric acid, deliquescent crystals of $2Hg(NO_3)_2.H_2O$ are formed. If the mother liquid be boiled, a compound $Hg(NO_3)_2.HgO.2H_2O$ is precipitated, and if this precipitate, or mercuric nitrate, be treated with an excess of cold water, $Hg(NO_3)_2.2HgO.H_2O$ is precipitated as basic mercuric nitrate. Thus, like mercurous nitrate, mercuric nitrate has a great tendency to form basic salts.

Lead nitrate, $Pb(NO_3)_2$.—Lead nitrate is formed by dissolving the metal, the oxide, carbonate, etc., in nitric acid. The salt is deposited in regular octahedral crystals isomorphous with barium nitrate. When heated lead nitrate decomposes as indicated above. The aqueous solution is faintly acid, and basic salts are formed when the aqueous solution is boiled with lead monoxide—$Pb(NO_3)OH$. Other basic salts are obtained by adding ammonia to a solution of lead nitrate.

§ 9 Nitrous Acid and the Nitrites

In making sodium or potassium nitrite by the action of heat on the corresponding nitrate, it is best to mix the nitrate with a mild reducing agent like metallic lead or iron filings. Thus by heating a mixture of lead filings with an equal weight of sodium nitrate in a crucible: $Pb + NaNO_3 = PbO + NaNO_2$. Digest the cold mass with water, filter and evaporate the solution to a small bulk, when sodium nitrite will separate on cooling. Most of the nitrites are very soluble in water, but silver nitrite is not very soluble in cold water. It is precipitated in crystalline needles when a solution of silver nitrate is added to a solution of sodium nitrite.

Nitrous acid can be made by adding hydrochloric or sulphuric acid to a solution of the nitrite: $NaNO_2 + HCl = NaCl + HNO_2$. If hydrogen

peroxide be added to a solution of ammonia, the latter is oxidized to nitrous acid $NH_3 + 3H_2O_2 = HNO_2 + 4H_2O$ Since an excess of ammonia is usually present, ammonium nitrite is formed When ammonium nitrite is heated, nitrogen is formed (p 555) The aqueous solution of the acid gradually decomposes at ordinary temperatures $3HNO_2 = HNO_3 + 2NO + H_2O$ The decomposition is much quicker when the solution is warmed Nitrous acid is only known in dilute solutions

The acid acts both as an oxidizing agent and as a reducing agent Thus, it *oxidizes* hydriodic acid or potassium iodide liberating iodine $2HI + 2HNO_2 = 2H_2O + 2NO + I_2$ A solution of potassium permanganate, however, is rapidly decolorized in the presence of sulphuric acid with the formation of manganous sulphate The permanganate is thus *reduced* by the nitrite solution

Constitution of nitrous acid—The formula HNO_2 is confirmed by electrical conductivity measurements. There is some difference of opinion which of the formulæ

$$\begin{matrix}O\\O\end{matrix}\!\!\geqslant N-H\,, \text{ or } \begin{matrix}O\\O\end{matrix}\!\!>N-H\,, \text{ or } O=N-OH$$

represents nitrous acid The difference between the first two can only be answered by evidence showing whether the nitrogen atom be ter- or quinquevalent. Nitrocellulose and the other compounds indicated on p 512, are in harmony with one of the first two formulæ, because in these compounds the group NO_2 acts as a monad radicle On the other hand, compounds like nitrosyl chloride, NOCl, nitrosyl fluoride, NOF, etc, agree with the third formula, because in these compounds the OH radicle is replaced by monad chlorine, fluorine, etc The evidence is thus in favour of a desmotropic or tautomeric structure discussed on p 425 Orthonitrous acid may be regarded as the final oxidation product of ammonia, where NH_3 becomes $N(OH)_3$ This orthonitrous acid is unknown even in combination Ordinary nitrous acid is metanitrous acid, and the nitrites are meta-salts

Identification of nitrites and nitrates—Dilute sulphuric acid decomposes all the nitrites in the cold Nitric oxide is formed, which gives brownish red fumes in the air $3HNO_2 = HNO_3 + 2NO + H_2O$ Nitrates do not give the brown fumes, unless they be heated with concentrated sulphuric acid. Potassium iodide is not decomposed by pure dilute nitric acid, whereas, a solution of a nitrite, when acidified with dilute sulphuric or acetic acid, becomes yellow or brown owing to the separation of iodine If a little starch paste be present, the solution will be coloured blue Many other oxidizing agents give the same coloration—ozone, hydrogen peroxide, chlorine, and ferric salts. Nitrates give the same coloration if a little zinc be added to the acidified solution owing to the reduction of the nitrates to nitrites A sensitive test for the nitrates is based upon the oxidation of ferrous salts by nitric acid $6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO$, and by nitrous acid $2FeSO_4 + H_2SO_4 + 2HNO_2 = Fe_2(SO_4)_3 + 2H_2O + 2NO$ In the cold, the nitric oxide forms a dark brown compound with the excess of ferrous salt To apply the test, dissolve the nitrate in as little water as possible Add a cold saturated solution of ferrous sulphate slightly acidified with sulphuric acid Pour concentrated sulphuric acid down the side of the tube If nitric acid be present, the zone of contact will be coloured dark brown With nitrites, the concentrated sulphuric acid need not be added

§ 10 Nitrous Oxide, or Nitrogen Monoxide

Molecular weight, $N_2O = 44.02$ Melting point $-102.7°$, boiling point $-89.8°$, critical temperature, $+36.5°$ Vapour density ($O_2 = 32$), 44.02, (air = 1) 1.5299 One litre under standard conditions weighs 1.9777 gram

Preparation.—Nitrous oxide, as we have seen, is produced when nitric acid, specific gravity 1.1, reacts with zinc or tin J Priestley discovered the gas in 1772, and he made it by reducing nitric oxide with moist iron filings, or potassium sulphide, etc The gas is also formed by heating hydroxylamine nitrite $NH_2OH.HNO_2 = 2H_2O + N_2O$ Nitrous oxide, however is rarely prepared by these methods for experimental work.

One most convenient mode of preparation is to heat dry ammonium nitrate in a flask fitted with a delivery tube (Fig 94) The salt melts at about 165°, and it begins to decompose at about 185° The decomposition proceeds quite rapidly between 200° and 240° Nitrous oxide and water are formed $NH_4NO_3 = 2H_2O + N_2O$ At 240° the decomposition is very vigorous, and the mixture may even explode A well dried mixture of ammonium sulphate and sodium nitrate is often preferred to ammonium nitrate because the decomposition then proceeds quietly and more uniformly $(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 4H_2O + 2N_2O$. When ammonium nitrate decomposes very rapidly, appreciable quantities of nitric oxide are formed (If required for special work, the gas must be purified from chlorine (formed from the chlorides contaminating the ammonium nitrate), by passing the gas through a solution of potassium hydroxide, and from nitric oxide, by passing the gas through a solution of ferrous sulphate)

Properties.—Nitrous oxide is a colourless gas with a faint smell 100 c c of water, at 760 mm pressure, dissolve 130 volumes of the gas at 0°, and 67 volumes at 20° Hence the gas is usually collected over hot water in order to lessen the loss due to its solubility in that liquid. The aqueous solution has a sweetish taste The gas is about four times as soluble in alcohol as in water

The gas condenses to a colourless limpid liquid at 0° under a pressure of thirty atmospheres. M. Faraday liquefied the gas in 1823 Liquid nitrous oxide can be purchased in steel cylinders The liquid boils at —89.3°, and freezes to a snow like mass when allowed to evaporate The solid melts at —102·7° The liquid forms a crystalline hydrate $N_2O.6H_2O$ with water Both the liquid and solid produce painful blisters when dropped on the hand If liquid nitrous oxide be mixed with carbon disulphide and placed in a vacuum, the temperature of the mixture falls to —140°

Nitrous oxide resembles oxygen in its behaviour towards combustibles. A brightly glowing splinter bursts into flame when plunged into the gas Burning phosphorus, sulphur, etc, burn vividly in nitrous oxide gas. When J Priestley discovered oxygen in 1774, he was already familiar with nitrous oxide, which he had discovered a couple of years previously Hence in describing the brilliancy of the flame of a burning candle in oxygen, he said "I got nothing like this remarkable appearance from any kind of air besides this particular modification of nitrous air" The burning body decomposes the nitrous oxide, unites with the oxygen, and leaves the nitrogen as a residue If sulphur be but feebly burning, its flame is

extinguished when plunged into nitrous oxide, probably because the temperature is not high enough to decompose the gas It is therefore easy to mistake nitrous oxide for oxygen One distinguishing test is to add a bubble of suspected gas to the nitric oxide if red fumes are produced the gas is oxygen Nitrous oxide does not give red fumes with nitric oxide Another test depends on the far greater solubility of nitrous oxide in alcohol than oxygen

When inhaled, nitrous oxide produces unconsciousness, and insensibility to pain Hence it has long been used as an anæsthetic for small surgical operations, dentistry, etc But owing to the unpleasant after effects sometimes produced, it is not used so much as formerly If the inhalation be long continued, it may produce death, while if but small quantities are inhaled, it may produce a kind of hysteria, or intoxication Hence the gas is sometimes called "laughing gas" As L Edgworth remarked (1799), after breathing the gas, "I burst into a violent fit of laughter, and capered about the room without having the power of restraining myself" and H. Davy wrote (1794) after breathing sixteen quarts of the gas, "I danced about the laboratory as a madman" The effects of the gas are not quite the same on different people

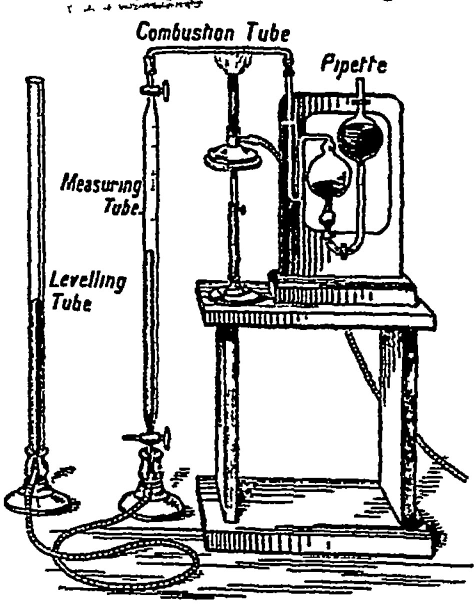


FIG 188 —Composition of Nitrogen Oxides

The formation of nitrous oxide is an endothermal reaction $2N + O = N_2O - 18$ Cals Nitrous oxide decomposes with an explosion if a fulminating cap be detonated in the gas. Nitrous oxide decomposes into its elements when heated, $2N_2O \rightarrow 2N_2 + O_2$ Two volumes of the gas furnish two volumes of nitrogen and one volume of oxygen —three volumes in all

Composition of nitrous oxide.—The oxygen can be withdrawn from nitrous oxide, by sodium or potassium, or barium sulphide, in an apparatus like that indicated in Fig 156 The equation cannot be given because of the uncertainty what particular oxide is formed. With potassium an oxide is formed which spontaneously absorbs oxygen when exposed to the air The following is a better way of conducting the experiment A hard glass or quartz tube about 3 mm bore, and 10–12 cm. long is filled with metallic copper made by reducing the granulated oxide in a current of hydrogen The copper is held in place by plugs of asbestos at each end This tube is mounted between Hempel's burette (p 94), and a two bulbed gas pipette, Fig 188 Both the burette and pipette are charged with mercury The upper bulb of the pipette is empty when the lower bulb is full of mercury, the mercury extends to a mark on the gauge tube of the pipette The burette contains a measured volume of nitrous oxide By opening the stopcock, and raising the levelling tube a slow current of the gas is led

over the red hot metallic copper into the pipette When the lower bulb of the pipette is nearly full of gas, return the gas to the burette, by lowering the levelling tube When the gas is cold, read its volume when the mercury in the measuring and levelling tubes is at the same level It will be found that although the gas has decomposed, and copper oxide[1] is formed, this has made no difference to the volume of the gas in the burette. This experiment proves that nitrous oxide contains its own volume of nitrogen Or one molecule of nitrous oxide contains one molecule of nitrogen, that is, two atoms of nitrogen and the formula of nitrous oxide must therefore be N_2O_n where n is to be determined

One gram molecule of nitrous oxide weighs	44 027 grams
One gram molecule of nitrogen weighs	28 020 ,,
Weight of oxygen in the molecule	16 007 ,,

Assuming that the small fraction here represents an experimental error, the number 16·007 can represent one and only one atom of oxygen, since the atomic weight of oxygen is 16 This means that the formula for nitrous oxide is N_2O The molecule is supposed to be constituted $\begin{matrix}N\\N\end{matrix}\!\!>\!O$ and the nitrogen atom is supposed to be tervalent, not univalent, as might be inferred by analogy with water H O H, but there are other possibilities, *e g* O=N≡N Nitrous oxide appears to be the anhydride of hyponitrous acid $N_2O + H_2O = H_2N_2O_2$, but nitrous oxide does not seem to react with water in this manner, although nitrous oxide is formed when concentrated sulphuric acid acts on hyponitrous acid $H_2N_2O_2 + H_2SO_4 = H_2SO_4 \cdot H_2O + N_2O$ Nitrous oxide has also been analyzed gravimetrically by determining the increase in weight of the copper (Fig 188), and also by heating electrically a weighed spiral of iron wire in the gas, and finding the increase in weight due to the absorption of oxygen, that is, to the formation of ferric oxide

EXAMPLE —1 1670 gram of nitrous oxide gave 0 4242 gram of oxygen; and hence the gas contains 0 7428 gram of nitrogen What is the formula of nitrous oxide? The gas contains 0 7428 gram of nitrogen per 0 4242 gram of oxygen Divide these numbers by the corresponding atomic weights, as indicated on p 61, and we get the atomic ratio N O = 2 1 Hence the formula is $(N_2O)_n$ But the density of nitrous oxide is 44 0074 This corresponds with the molecule N_2O when the atomic weights of oxygen and nitrogen are respectively 16 and 14 01

A mixture of equal volumes of nitrous oxide and hydrogen explodes when sparked, so that

$$\underset{2\text{ vols}}{N_2O} + \underset{2\text{ vols}}{H_2} = \underbrace{N_2 + H_2O_{\text{liquid}}}_{2\text{ vols}}$$

The water condenses to a liquid, and hence its volume is negligibly small. The explosion is not so violent as with electrolytic gas, p 52 Since this method is used for determining the amount of oxygen admixed with nitrogen, the process may be described in a little more detail

Analysis of mixtures of nitrogen and oxygen —Suppose that 30 c c of nitrous oxide be transferred to a Hempel's burette charged with mercury (p 94), and then 40 c c of hydrogen be added Connect the Hempel's burette with Hempel's explosion pipette, Fig 189, by means of a piece of

[1] Below 350° cuprous oxide Cu_2O, not CuO, is formed, above 350°, CuO is produced

capillary tube and two pieces of thick walled pressure tubing. The explosion pipette consists of a thick-walled glass bulb in which are fused two platinum wires with tips about 2 mm. apart This explosion bulb is connected with another bulb by means of a glass tube and stopcock The upper end of the explosion bulb ends in a U-shaped gauge tube The explosion pipette is charged with mercury in such a way that the upper bulb is empty when the lower bulb is full of mercury, and the mercury extends to a mark on the gauge tube. Open the two stopcocks and raise the levelling tube of the burette so as to transfer the gas from the burette to the explosion pipette Allow a little mercury to pass into the pipette from the burette to make sure that all the gas has been transferred to the pipette Close both stopcocks, and pass a spark across the platinum terminals After the explosion, open both stopcocks, and transfer the gas from the pipette to the burette by depressing the levelling tube until the level of the mercury in the burette is in its former position The volume of the water formed during the explosion is negligibly small in comparison with the gases from which it is formed. Bring the mercury to the same level in both tubes and read the volume of the gas in the burette. Suppose

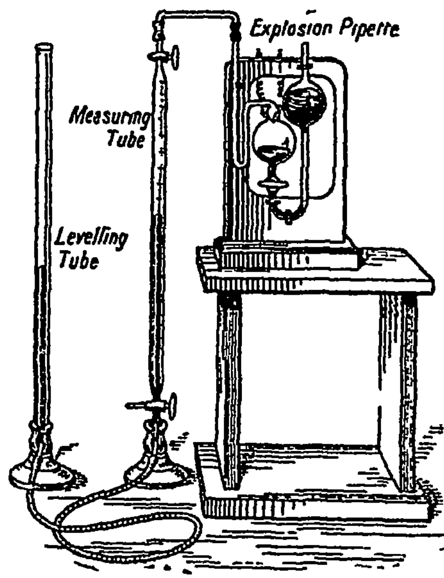


FIG 189 —Analysis of Gases by Explosion

BEFORE EXPLOSION	Volume of nitrous oxide	30 c c
	Volume of hydrogen added	40 c c
	Total volume	70 c c
AFTER EXPLOSION	Total volume of mixture	40 c c
	Contraction	30 c c

If 30 c c of hydrogen have been converted into water, 15 c c of oxygen must have been used for this reaction Hence 15 c c of oxygen must have been taken from the nitrous oxide Hence 10 c c of hydrogen were added in excess of what was actually required Consequently, 30 c c of nitrogen remain mixed with 10 c c of hydrogen Some oxides of nitrogen are formed during the explosion, and these dissolve in the water forming nitric and nitrous acids This causes rather low results for nitrogen.

§ 11 Nitric Oxide, or Nitrogen Dioxide

Molecular weight, NO = 30 01 Melting point, $-167°$, boiling point, $-150°$; critical temperature, $-94°$ Vapour density ($H_2 = 2$), 29 88, (air = 1) 1 039

History —J Priestley (1772) is generally regarded as the discoverer of nitric oxide, although J Mayow (1669) made it by treating iron

with nitric acid, and R Boyle (1671) noted that it formed reddish fumes in contact with air J B van Helmont (c 1600) knew the gas, although his descriptions seem to confuse it with carbon dioxide, probably because he had one name—gas sylvestre—for a number of different gases.

Preparation—Nitric oxide is prepared by the action of nitric acid, specific gravity 1 2, upon metallic copper or mercury The copper turnings are placed in a two necked Woulfe's bottle (Fig 9) or a Kipp's apparatus (Fig 12) The bottle is about one fourth filled with water, and about the same volume of concentrated nitric acid is added. A rapid evolution of gas occurs. The gas should be collected as soon as possible because when the reaction has been in progress some time, particularly if the temperature rises during the reaction, nitrous oxide and nitrogen may appear with the nitric oxide, as indicated on p 513 The results are better if a little sodium nitrite, say, two per cent, be added to the mixture in the Woulfe's bottle

A purer gas is obtained by reducing potassium nitrate with ferrous sulphate acidified with sulphuric acid, or ferrous chloride acidified with hydrochloric acid $KNO_3 + 3FeCl_2 + 4HCl = 3FeCl_3 + KCl + 2H_2O + NO$ A mixture of 12 grams of potassium nitrate with 100 grams of ferrous sulphate is introduced into a flask, Fig 94, and mixed with 100 c c of water and 60 c c of sulphuric acid A steady stream of nitric oxide is evolved when the mixture is warmed According to L. W Winkler (1889) highly pure nitric oxide can be made by dropping a 50 per cent solution of sulphuric acid upon a mixed solution of potassium iodide and sodium nitrite in the apparatus depicted Fig 47

Properties—Nitric oxide is a colourless gas a little heavier than air When brought in contact with air, it immediately combines with the oxygen forming brownish red fumes of nitrogen peroxide No other gas gives red fumes when exposed to the atmosphere or to oxygen gas Hence it is not possible to describe the smell, and the physiological action of this gas If the two gases—nitric oxide and oxygen—be thoroughly dried, no combination occurs. If dry nitric oxide be passed into liquid oxygen or liquid air greenish flocks of nitrogen hexoxide are formed Analyses give results corresponding with the empirical formula NO_3 Hence the reaction is represented $NO + O_2 = NO_3$ Nitrogen hexoxide decomposes spontaneously into N_2O_3, N_2O_4, and a little free oxygen, at temperatures a little above the boiling point of oxgyen E Müller (1914) considers that the alleged hexoxide is really a mixture of N_2O_4, N_2O_3 and NO

At 0° and 760 mm pressure, 100 volumes of water dissolve 7 3 volumes of the gas, and at 20°, 4 6 volumes Nitric oxide dissolves in a solution of ferrous sulphate A "compound" of nitric oxide and ferrous sulphate appears to be formed This imparts a dark brown colour to the solution The "compound" is decomposed when heated to about 60°, and nitric oxide is evolved. It is not very clear if a true compound is formed between the nitric oxide and the ferrous salt, because its composition seems to vary with the temperature of formation Thus at 8° the composition corresponds with $3FeSO_4$ 2NO, from 8° to 25°, about $2FeSO_4$ NO, and above 25°, $5FeSO_4$ NO With these facts, and the law of constant composition before us, we cannot very well say that ferrous sulphate forms a true chemical compound with nitric oxide, p 473 Ferrous, cobaltous, nickelous, manganous, and chromous chlorides give similar results Nitric oxide

also dissolves in nitric acid forming a coloured solution ranging in tint, from brown, to yellow, to green, to blue.

Nitric oxide is difficult to liquefy At $-93.5°$, a pressure of 71.2 atmospheres is required to liquefy the gas The liquid is colourless if air be excluded, otherwise the liquid may be tinted green or blue The liquid boils at $-150°$, and the white solid melts at $-167°$

Nitric oxide is not combustible, and it only supports combustion under special conditions, that is when the temperature is raised sufficiently to decompose the gas. The flame of feebly burning phosphorus is extinguished, but if the phosphorus be burning vigorously, combustion is continued in the gas. Burning sulphur is extinguished, but if the sulphur be boiling when it is plunged in the gas combustion sometimes continues Potassium also burns in the gas forming a mixture of nitrites and nitrates Sodium can be heated in a tube containing the gas without the metal burning A mixture of nitric oxide with hydrogen can be sparked without explosion, but if the mixture be passed through a hot tube, decomposition takes place $2H_2 + 2NO = 2H_2O + N_2$ If the tube contains platinized asbestos or finely divided nickel or copper (reduced from the oxides) ammonia gas is formed $2NO + 5H_2 = 2H_2O + 2NH_3$ *A slow current* of nitric oxide is mixed with an excess of hydrogen in the apparatus illustrated in Fig 190, which explains itself The dry hydrogen comes from a Kipp's apparatus The ammonia and the excess of hydrogen can be passed through a dilute solution of hydrochloric acid or sulphuric acid to form an ammonium salt, a red litmus paper held in the stream of gas will be coloured blue

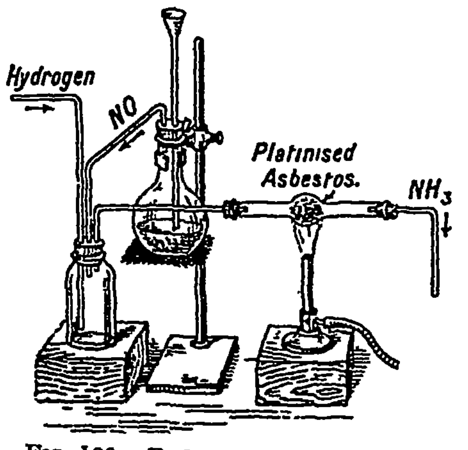


FIG 190—Reduction of Nitric Oxide to Ammonia

Decomposition —When nitric oxide is exposed to the shock of a detonation from mercury fulminate, the gas decomposes into its elements. The experiment can be made by exploding a percussion cap by means of an electric spark in a tube of the gas Nitric oxide, however, is one of the most stable of the nitrogen oxides It does not decompose appreciably when heated until the temperature reaches 500° The reaction $2NO \rightleftharpoons O_2 + N_2$ is reversible as indicated on p 509 so that at still higher temperatures, say, 3000°, over 4 per cent of the mixture of nitrogen and oxygen will combine to form nitric oxide This behaviour is characteristic of endothermal reactions, and $N + O = NO - 21.6$ Cals.

Nitric oxide *reduces* potassium permanganate, hydriodic acid, silver oxide, nitric acid, etc, in the cold, and it *oxidizes* potassium and barium sulphides, etc., when warmed.

Composition —The composition of nitric oxide may be established by the methods employed for nitrous oxide The residual nitrogen occupies half the volume of the original gas Hence one molecule of nitric oxide contains half a molecule of nitrogen, that is, one atom The formula is

S

therefore NO_n, where n has to be determined The density of the gas is 29 88 ($H_2 = 2$) Hence,

One gram molecule of nitric oxide weighs	29 88
One half gram molecule of nitrogen weighs	14 01
Equivalent weight of oxygen	15 88

This number, 15 88, can represent one and only one atom of oxygen, atomic weight 16 The formula must, therefore, be NO The vapour density agrees with this Hence the term nitrogen dioxide for this gas appears to be a misnomer The name nitrogen dioxide was given because nitric oxide contains twice as much oxygen for the same quantity of nitrogen as nitrogen monoxide—N_2O

√ EXAMPLE —R W Gray (1905) found that 0 6430 gram of nitric oxide, when passed over hot finely divided nickel increased the weight of the nickel 0 3430 gram, and the liberated nitrogen when condensed at the temperature of liquid air in cocoanut charcoal, furnished 0 3001 gram of nitrogen What is the formula of nitric oxide taking P A Guye and C Davila's (1905) number 1 3402 for the density of nitric oxide when air is unity, or 30 0124 when oxygen is 32 ? Divide 0 3430 by 16, and 0 3001 by 14 01 We get the atomic ratio 0 02144 0 02143, which is very nearly as 1 1 If the formula be NO, the vapour density is 30 01 This agrees with the observed result

If nitrogen be a triad, and oxygen a dyad, there must be one free valency in the graphic formula, —N=O The facts are, if oxygen is bivalent, nitrogen behaves as if it were also bivalent The ready way in which nitric oxide unites with other elements by direct addition rather lends itself to the idea that nitric oxide has a free valency Witness the direct combination of nitric oxide with oxygen at ordinary temperatures, and the direct combination of nitric oxide with chlorine and fluorine forming respectively nitrosyl chloride, NOCl, and nitrosyl fluoride, NOF The NO group is sometimes called nitrosyl and compounds containing NO as a monad radicle, nitrosyls In this sense, nitrogen peroxide may be regarded as nitrosyl oxide, NO O, and nitrous acid, nitrosyl hydroxide, NO—OH.

Nitrosyl chloride, NOCl, can be prepared in many other ways. *E g* by the action of phosphorus pentachloride, PCl_5, upon potassium nitrite $PCl_5 + KNO_2 = KCl + POCl_3 + NOCl$, see also aqua regia, p 513 Nitrosyl chloride is an orange yellow gas which condenses to an orange coloured liquid at —8°, and freezes to lemon coloured crystals at —65° It is decomposed by water into nitrous and hydrochloric acids $NOCl + H_2O = HNO_2 + HCl$. It has no action on gold and platinum, but it attacks mercury, forming mercurous chloride, HgCl, and nitric oxide The density of the gas at 0° is 65 456

12 Nitrogen Peroxide or Nitrogen Tetroxide.

Molecular weight, $NO_2 = 46\ 01$, $N_2O_4 = 92\ 02$ Melting point, —9°, boiling point, +26° Vapour density depends upon the temperature

History—As indicated in discussing nitric oxide, R Boyle (1671) knew that nitric oxide formed red fumes in air, and since nitrogen peroxide is always formed during the preparation of nitric acid, nitrogen peroxide must have been recognized as a gas whenever nitric acid was made J L Gay-Lussac (1816) first made its composition clear

Preparation —As indicated above, this gas is formed when one volume of oxygen is mixed with two volumes of nitric oxide $2NO + O_2 = 2NO_2$. If the gas be led through a freezing mixture, the peroxide condenses either as a liquid or as a solid. Similarly, if the products obtained by heating a metallic nitrate (p 517), say, lead nitrate, be similarly treated, this compound also condenses as a more or less impure liquid Perhaps the best way of making nitrogen peroxide is to put, say, 200 grams of coarse lumps of arsenic trioxide, As_2O_3, into a flask, and add 250 grams of nitric acid (specific gravity 1 4) Heat the mixture on a sand-bath, and lead the gases through a tower packed with glass wool, Fig 191, and finally into a U-tube surrounded by a freezing mixture of ice and salt A dark blue liquid is condensed This is a mixture of nitrogen peroxide with nitrogen trioxide, etc When the evolution of gas has ceased, pass a current of air or oxygen through the condensed liquid while still in the freezing mixture until the liquid becomes yellowish-brown In special cases, the yellowish-brown liquid can be further purified by mixing it with a large quantity of phosphorus pentoxide and strong nitric acid Decant the nitrogen peroxide from the syrupy liquid, and redistil the mixture by warming in hot water, and passing the gases through tower and condensing tube as in Fig 191

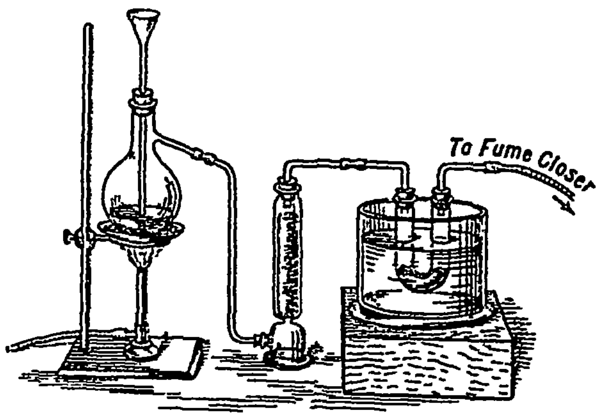


FIG 191 —Preparation of Nitrogen Peroxide

Action of heat on nitrogen peroxide — At low temperatures nitrogen peroxide forms colourless prismatic crystals. The crystals melt at $-9°$, but owing to "undercooling" a temperature in the vicinity of $-30°$ is sometimes needed to solidify the liquid As the temperature of the liquid rises, it begins to acquire a pale greenish-yellow tint, which becomes deeper and deeper, until, at 10°, the liquid is distinctly yellow, at 15°, orange, and at 26°, the liquid boils and forms a reddish-brown vapour. The colour of the vapour becomes deeper and deeper until, at 40°, it is dark chocolate brown, and almost opaque, at 140°, the vapour is almost black On cooling the vapour, the same changes occur in the reverse order The effect seems to be connected with a change in the vapour density of the compound. The vapour density for N_2O_4 is 92 02, and for NO_2, 46 01 The actual value of this constant passes from 84 7 at -72 6° and 115 4 mm pressure, to 46 0 at 140° and 760 mm pressure, and for intermediate temperatures

Temperature	26 7°	60 2°	100 1°	135 0°	140°
Density ($H_2 = 2$)	76 6	60 2	48 6	46 2	46 0
NO_2 molecules	20 0	50 0	79 2	99 0	100 0 per cent.

Given the vapour density of the gas and the vapour density of each component, it is possible to calculate, by the subjoined method the

relative proportions of N_2O_4 and NO_2 molecules at any given temperature Let x denote the fraction of the total volume of the gas present as NO_2, then $1-x$ will represent the fraction of the total volume present as N_2O_4 The vapour density of NO_2 is 46, and of N_2O_4, 92 Hence if the molecular weight of the gas be M, that is, the vapour density, hydrogen 2, we shall have $M = 46x + (1-x)92$ Hence unit volume of the gas will contain

$$x = \frac{92 - M}{46} \text{ volumes of } NO_2$$

EXAMPLE —What proportion of nitrogen peroxide is present in 100 volumes of the gas when the vapour density is 76 6 ($H_2 = 2$) ? Here, $M = 76\ 6$, and $x = 0\ 333$, that is, the gas contains 33 3 per cent by volume of NO_2

In the preceding example, for every 0 333 volume of NO_2 there is 0 667 volume of N_2O_4 Each molecule of the latter weighs twice as much as the former, so that the total weight of the gas must be $0\ 333 + 2 \times 0\ 666 = 1\ 667$ units when there is 0 333 unit of NO_2 molecules present Hence there will be $0\ 333 - 1\ 667 = 0\ 20$ unit of NO_2 by weight, or 20 per cent of the total weight of the gas will be present as NO_2 molecules. The percentage proportion of NO_2 molecules in the gas at different temperatures is indicated in Fig 192 It is therefore probable (1) Colourless nitrogen peroxide consists of N_2O_4 molecules, and coloured nitrogen peroxide of NO_2 molecules, (2) At low temperatures, the molecules are mainly N_2O_4, and at high temperatures, NO_2, (3) The dissociation of N_2O_4 into NO_2 begins when the compound is in the liquid state, and (4) Nitrogen peroxide below 140° is a mixture of N_2O_4 and NO_2 molecules, and just above 140°, of NO_2 molecules alone

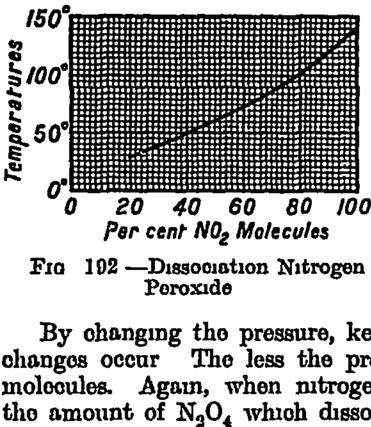


FIG 192 —Dissociation Nitrogen Peroxide

By changing the pressure, keeping the temperature constant, similar changes occur The less the pressure, the greater the number of NO_2 molecules. Again, when nitrogen peroxide is diluted with chloroform, the amount of N_2O_4 which dissociates increases with dilution as well as with rise of temperature The freezing point of a solution of nitrogen peroxide in acetic acid corresponds with the molecule N_2O_4

The facts indicate that we are here dealing with two opposing reactions (p 97) represented

C_1

$$2NO_2 \rightleftharpoons N_2O_4$$

The velocity of the right to left transformation is proportional to the concentration of the N_2O_4 molecules (p 96), that is, the rate of dissociation of the N_2O_4 molecules is equal to k_1C_1 where C_1 denotes the concentration of the N_2O_4 molecules expressed in, say, gram molecules per unit volume, and k_1 is the affinity constant, p 97 Similarly, the rate of combination of the $NO_2 + NO_2$ molecules is proportional to the concentration of the reacting NO_2 molecules per unit volume, that is, to $kC \times C$, where C denotes the concentration of the reacting NO_2 molecules. For

equilibrium, these two opposing reactions will be the same, and we shall have

$$kC^2 = k_1C_1, \text{ or } \frac{C^2}{C_1} = \frac{k_1}{k}, \text{ or } \frac{C^2}{C} = K$$

where K is the so called equilibrium constant. The experimental results in all cases indicate that the equation just obtained $C^2 = KC_1$ represents the condition of equilibrium of the gas with respect to the distribution of the two different kinds of molecules at different temperatures and pressures The numerical values of the affinity constants change with the temperature, but its value is constant for differences of pressure, and the observed results agree with the formula $C^2 = KC_1$

At about 500°, an appreciable number of the dark brown molecules of NO_2 begin to dissociate into a colourless mixture of nitric oxide and oxygen $2NO_2 = 2NO + O_2$ (*cf* p 525) The action of heat on nitrogen peroxide may therefore be represented by the equations

$$\underbrace{\underset{\text{Colourless}}{N_2O_4}}_{\text{about }20^\circ} \rightleftharpoons \underbrace{\underset{\text{Dark brown}}{2NO_2}}_{\text{Between }140^\circ\text{ and }300^\circ} \rightleftharpoons \underbrace{\underset{\text{Colourless}}{2NO + O_2}}_{\text{Above }500^\circ}$$

Properties —Nitrogen peroxide is a poisonous gas, and soon produces headache and sickness if but a little is present in the atmosphere

Nitrogen peroxide is not combustible, and it extinguishes the flame of a taper Phosphorus, sulphur, and carbon, if burning vigorously, may continue burning in the gas, but only when the temperature of combustion is sufficiently high to decompose the gas. Nitrogen peroxide is an energetic oxidizing agent Phosphorus, carbon, potassium, mercury, copper, etc, when heated in the gas, are oxidized, while the gas is decomposed The gas liberates iodine from potassium iodide, and it reduces permanganates

Action of water —Nitrogen peroxide is decomposed by water At low temperatures, a mixture of nitric and nitrous acid are formed $N_2O_4 + H_2O = HNO_3 + HNO_2$, and with aqueous solutions of the alkalies, the corresponding salts are obtained When nitrogen peroxide is dissolved in water, the solution passes through a series of colour changes—blue, green, orange This is due to the gradual solution of the nitrogen peroxide in the nitric acid. If sufficient water be present, the solution finally becomes colourless With warm water, the nitrous acid decomposes into nitric acid, and nitric oxide $3NO_2 + H_2O = 2HNO_3 + NO$

J Priestley (1772) analyzed air by taking advantage of the fact that when nitric oxide is added to air, nitrogen peroxide is formed, and the red fumes are dissolved by potassium hydroxide Hence, if nitric oxide be gradually added to a known volume of air, in presence of this alkali, the nitrogen peroxide is absorbed. The residual gas is nitrogen, all the oxygen is removed by the nitric oxide This method is not often used because other processes are less troublesome The formation of acid when nitrogen peroxide dissolves in water, and the formation of nitrogen peroxide by the action of oxygen on nitric oxide, may be illustrated by an apparatus fitted up as shown in Fig 193 A little water is placed in the globe The globe is then filled with nitric oxide The lower vessel is filled with water tinted with blue litmus Oxygen is led slowly into the globe through the side tube Red fumes of nitrogen peroxide are formed, this gas is absorbed by the water and the pressure is reduced The coloured water rises from

the dish into the globe to restore equilibrium The blue litmus is coloured red by the acid formed in the globe If everything is properly regulated, the globe will be nearly filled with water, and the first rush of water will appear as a miniature fountain inside the globe

Nitroxyl —Nitrogen peroxide unites directly with copper, cobalt, nickel, and iron, forming the so called *nitro-metals* For instance, finely divided copper obtained by reducing the oxide in a stream of hydrogen, absorbs about 1,000 times its volume of nitrogen peroxide, much heat is evolved, and brown solid copper nitroxyl, Cu_2NO_2, is formed The group NO_2 thus behaves as if it were a monad radicle The radicle NO_2 is called nitroxyl, and compounds containing the NO_2 group are called nitroxyls At 90°, copper nitroxyl is decomposed into metallic copper and nitrogen peroxide

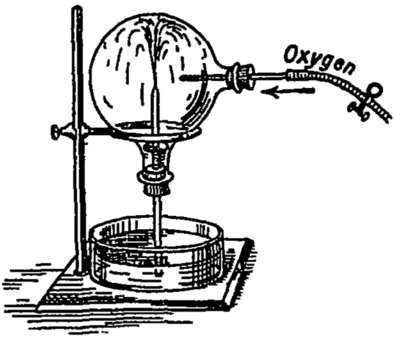


FIG 193 —Nitrogen Peroxide Fountain.

Composition —In gaseous nitrogen peroxide, NO_2, we have to assume either that nitrogen is quadrivalent, O=N=O, or else that nitrogen is quinquevalent, O=N=O, with a free valency There is no free valency difficulty with the compound N_2O_4, because two nitrogen atoms are here either quinquevalent, or one is quinquevalent, and the other tervalent

$$\begin{matrix}O\\O\end{matrix}\!\!>\!\!N-N\!\!<\!\!\begin{matrix}O\\O\end{matrix}\,, \text{ or } \quad O=N-O-N\!\!<\!\!\begin{matrix}O\\O\end{matrix}$$

The action of cold water on the peroxide forming nitrous and nitric acid, seems to favour the second formula. Nitrogen peroxide appears to be a mixed anhydride of both nitric and nitrous acids. The composition of nitrogen peroxide can be established first by showing that it is formed by the union of equal molecules of oxygen and nitric oxide, by the apparatus indicated Fig 188, and by vapour density determinations.

§ 13 Nitrogen Trioxide

Molecular weight, $N_2O_3 = 76\ 02$ Melting point, −111°, boiling point, 2°—with decomposition The vapour density show that the molecule decomposes

When a mixture[1] of nitric oxide and nitrogen peroxide is passed through a tube cooled to about −30°, a more or less impure form of nitrogen trioxide—N_2O_3—condenses to a bluish liquid. As soon as the temperature rises, the liquid dissociates $N_2O_3 = NO + NO_2$, nitric oxide escapes, and leaves a residual yellow liquid of nitrogen peroxide The melting-point curve of mixtures of nitric oxide and nitrogen peroxide indicates the formation of a compound N_2O_3 melting at −103° If more nitrogen peroxide be present, the melting point falls to the eutectic temperature

[1] The gas obtained by the action of nitric acid upon arsenic trioxide (p 527), is a mixture of nitric oxide and nitrogen peroxide in nearly the right proportions The same remark applies to the gas formed by the decomposition of a 20 per cent. solution of sodium nitrite with concentrated sulphuric acid

−112°. The trioxide is also produced by the direct union of solid nitrogen peroxide with nitric oxide, and by the action of oxygen on liquid nitric oxide. The trioxide, not the peroxide, appears to be formed when nitric oxide unites with oxygen at temperatures below −100°. Nitrogen trioxide is also formed when electric discharges are passed through liquid air. In this case, the solid trioxide separates as a pale blue amorphous powder which remains as a residue after the air has all evaporated. The solid melts between −103° and −111° to a deep indigo blue liquid, which commences to decompose immediately the temperature rises above −21°.

The composition of nitrogen trioxide has been established by passing the products of its decomposition over heated copper, and weighing the copper oxide and the nitrogen (p. 521). It is supposed to be represented either by—

$$O<\begin{matrix}N=O\\N=O\end{matrix}, \text{ or, } O=N-N\lll\begin{matrix}O\\O\end{matrix}$$

The former agrees best with the fact that nitrogen trioxide forms nitrous acid in contact with a little cold water: $N_2O_3 + H_2O = 2HNO_2$. Hence the gas is sometimes called nitrous anhydride. If the water is warm the nitrous acid decomposes, and nitric oxide and nitric acid are formed. According to H. B. Baker (1907) if the liquid be thoroughly dried, it vaporizes without dissociation, forming a gas which has a vapour density never below 76 ($H_2 = 2$), but generally much above that number (N_4O_6). If this be confirmed, it is the only direct evidence we have of the existence of the gaseous nitrogen trioxide. The freezing point method of determining the molecular weight in acetic acid furnished W. Ramsay (1888) with numbers between 80·9 and 92·7—theory for N_2O_3 requires 76·02. Hence the liquid is partly polymerized. Many reactions formerly said to yield the trioxide really give a mixture of nitric oxide and nitrogen peroxide.

Recapitulation.—Before dismissing the nitrogen oxides it will be found instructive to draw up a table of their comparable properties—omitting the hexoxide.

TABLE XXXIII.—PROPERTIES OF THE NITROGEN OXIDES.

	Nitrogen monoxide	Nitric oxide	Nitrogen trioxide	Nitrogen peroxide	Nitrogen pentoxide
Formula	N_2O	NO	N_2O_3	N_2O_4	N_2O_5
Atomic ratio N : O	2 : 1	2 : 2	2 : 3	2 : 4	2 : 5
State of aggregation	Gas	Gas	Gas	Liquid	Solid
Colour	Colourless	Colourless	Reddish brown	Colourless	White
Melting point	−102·7°	−167°	−111°	−9°	c. 30°
Boiling point	−89·8°	−150°	—	+26°	c. 47°
Vapour density (H_2 = 2)	44	29·88	Decomposes	Varies with temperature	—
Corresponding acid	HNO	None	HNO_2	None	HNO_3

Nitrogen sulphides.—The sulphides have not been so thoroughly investigated as the oxides When a solution of dry ammonia in benzene is treated with sulphur chloride, or when liquid ammonia acts on sulphur, long orange red monoclinic crystals of nitrogen tetrasulphide can be obtained The crystals have a characteristic smell, and decompose explosively at about 185°, although they may be sublimed without decomposition in vacuo at 100° The molecular weight by freezing and boiling point methods—solution in carbon disulphide or benzene—corresponds with the formula N_4S_4 It is decomposed by cold water, forming ammonia and sulphuric and thiosulphuric acids It forms addition compounds with chlorine, bromine, sulphur chloride, etc, *e g* N_4S_4Cl, $N_4S_4Br_4$, $N_4S_4Br_6$ When it is sublimed in vacuo over silver gauze, a *blue polymeride* N_4S_4 is formed The constitution of the sulphide is unknown, but it has been referred to

$$S{=}S\begin{matrix}\diagup N{-}S{\equiv}N\\ \diagdown N{-}S{\equiv}N\end{matrix} \quad \text{or} \quad \begin{matrix}S{=}N{-}S{-}N\\ S{=}N{-}S{-}N\end{matrix}$$

A deep red liquid is formed when the tetrasulphide is treated with carbon disulphide at 100° The liquid solidifies between 10° and 11° to a mass resembling iodine The liquid is thought to contain nitrogen pentasulphide, N_2S_5

Questions

1 How would you prove that nitrous acid may act both as an oxidizing and as a reducing agent?—*London Univ*

2 Give illustrations of the behaviour of different metals towards nitric acid—*Aberdeen Univ*

3 Calculate the percentages of nitrogen and oxygen in the oxides of nitrogen and show what fundamental law of chemical combination they illustrate (Ca = 40, C = 12, N = 14)—*Princeton Univ, U S A*

4 30 c c of a compound of nitrogen and oxygen were exploded with an equal volume of hydrogen, after the explosion 30 c c of a gas which was pure nitrogen remained What is the composition (by volume) of the compound? Show from the experimental evidence that the gas could not have been a mixture of oxygen and nitrogen—*Univ, North Wales*

5 What is the action of concentrated nitric acid on (*a*) tin, (*b*) iodine; (*c*) sulphurous acid solution?—*St Andrews Univ*

6 Knowing that ammonium nitrate when heated gives nitrous oxide, what gas would you expect to be produced when ammonium nitrite is heated?—*R Galloway*

7 What is observed and what products are obtained when each of the following nitrates is heated until any decomposition which occurs is complete Copper nitrate, mercuric nitrate, ammonium nitrate, sodium nitrate? How could nitrogen be isolated from one of these nitrates?—*Sheffield Univ*

8 The weight of a shilling (British coinage containing 7 5 per cent of copper) is 6 grams How would you prepare pure silver nitrate from it, and how much would it yield theoretically?—*Oxford Senior Locals*

9 Outline the operations necessary for the production of liquid nitrogen peroxide from dry lead nitrate Describe carefully the changes in colour observed when nitrogen peroxide is heated until it becomes colourless, and subsequently cooled What explanation can be given of these changes?—*Sheffield Univ*

10 Give the preparation and properties of nitric oxide Show how the formula of the gas may be deduced from the following data—15 6 c c of the gas passed over heated copper give 7·8 c.c of nitrogen; the weight of nitric oxides which fills a certain globe is 3 75 grams, the weight of an equal volume of hydrogen being 0 25 gram.—*Cambridge Senior Locals*

11 Describe two examples of reactions which may be brought about by (*a*) the electric current, (*b*) the silent electric discharge, (*c*) the electric spark, and in any two instances describe exactly how the reaction may be carried out experimentally—*London Univ*

CHAPTER XXVIII

Compounds of Nitrogen and Hydrogen

§ 1 Ammonia—Occurrence and Preparation

Molecular weight, $NH_3 = 17.03$ Melting point, $-78°$, boiling point, $-33.5°$, critical temperature, $132.9° \pm 0.1°$ Vapour density ($H_2 = 2$), 16.97, (air = 1), 0.5971 One litre weighs 0.77079 gram under normal conditions

History—Ammonia was known to the early chemists, and Geber describes the preparation of ammonium chloride by heating urine and common salt Hence the alchemists' term—*spiritus salis urinæ* Ammonium chloride was first brought to Europe from Egypt, where it was prepared from the "soot" obtained by burning camel's dung The name ammonia seems to be connected somehow with the Egyptian sun-god—Ra Ammon, ammonium salts must have been known to the early Egyptian priests The term *sal ammoniac* was one of the early names for ammonium chloride, the equivalent term *sal armoniacum* which appears in the translations of Geber's writings, and which was used for some time afterwards, was probably a mis spelling, since the term "salt of Armenia"—*sal armoniacum*—was applied to common salt and to native sodium carbonate S Hales (1727) noticed that when lime was heated with sal ammoniac in a retort arranged to collect the gas over water, no gas appeared to be given off, on the contrary, water was sucked into the retort, when J Priestley (1774) tried the experiment with a mercury gas trough, he obtained ammonia gas which he called "alkaline air" C L Berthollet (1785), H. Davy (1800), and others established the composition of the gas

Occurrence—Small quantities of ammonia occur in atmospheric air and in natural waters. It is produced by the action of putrifying bacteria (p 506) on organic matter in the soil, etc The odour of ammonia can often be detected near stables. Ammonium salts are also deposited on the sides of craters and fissures of the lava streams of active volcanoes, and with boric acid in the fumaroles of Tuscany

Preparation—Ammonia can be obtained by reducing nitric acid, nitrates, or nitrites with nascent hydrogen (p 514) For instance, by boiling a mixture of 25 grams of sodium hydroxide in 70 c c of water, 20 grams of zinc turnings, a piece of bright sheet iron, and 5 grams of nitric acid in a half-litre flask, ammonia gas is slowly evolved The reduction of the nitric acid by the hydrogen liberated by the action of zinc on the alkaline solution (p 92) is rather too slow to make this a suitable process for making ammonia for experiments with the gas The reaction, however,

is rather important because upon it is based a method for determining the quantity of nitrites and nitrates in potable water

When ammonia gas is required for the laboratory, it may be obtained from a cylinder of liquid ammonia, by boiling commercial aqua ammonia in a flask—Fig 194, or by heating an intimate mixture of commercial ammonium chloride or ammonium sulphate with twice its weight of quicklime, CaO, or slaked lime, $Ca(OH)_2$ The reaction is represented $2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3$ Ammonia combines with the ordinary drying agents—calcium chloride, sulphuric acid, phosphorus pentoxide—and accordingly these agents must not be used with the idea of drying the gas A tower of quicklime, indicated in Fig 194, is generally employed If a mixture of ammonium chloride and quicklime is to be heated, a copper flask, without the tube funnel, Fig 194, is preferable to glass since steam is liable to condense on the walls of the flask, trickle down, and crack the hot glass Otherwise the disposition of the apparatus is similar

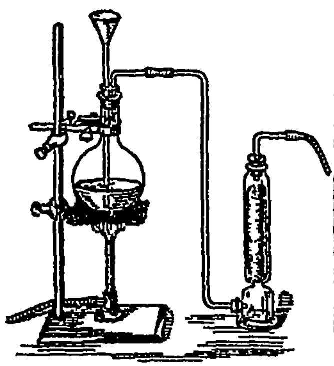


FIG 194 —Preparation of Ammonia

Ammonia is formed during the action of water on some of the metallic nitrides—compounds of the metals, magnesium, calcium, lithium, aluminium, etc, with nitrogen For instance, with hot water $Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$, and $AlN + 3H_2O = Al(OH)_3 + NH_3$, etc The action of superheated steam on calcium cyanamide (*q v*) also furnishes ammonia $CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$ The yield is 99 per cent of that indicated by this equation The process appears likely to have a commercial future

Ammonia is formed when nitrogenous compounds — coal, leather, bones, etc — are heated in closed vessels The old term for ammonia—*spirits of hartshorn*—refers to an old custom of preparing ammonia by heating hoofs and horns in closed vessels. The formation of ammonia by heating nitrogenous compounds in closed vessels is particularly noticeable if the organic matter be heated with soda lime—that is, quicklime slaked with a concentrated solution of sodium hydroxide In fact, this is the principle of one of the standard methods for the determination of nitrogen in organic matter The ammonia is absorbed in sulphuric acid Most of the ammonia of commerce is derived from the ammoniacal liquid obtained as a by product in the manufacture of coal gas (*q v*), in the manufacture of iron in the blast furnace (*q v*), and of producer gas This liquid is boiled with milk of lime, and the ammonia which is evolved is absorbed by dilute sulphuric acid—$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$ The ammonium sulphate so obtained crystallizes without evaporation when a sufficient concentration has been attained It is removed by perforated ladles and recrystallized, or heated with milk of lime, and the resulting gas absorbed in distilled water to form the *aqua ammonia* of commerce The solution of ammonia gas in water is conventionally styled "ammonia"

Nitrogen and hydrogen unite directly when a mixture of the two gases is subjected to electric sparks (Fig 155) The reaction appears to stop

when about 2 per cent of ammonia has been formed, and 98 per cent of gas remains uncombined The same result is obtained if ammonia gas be exposed to the electric sparks, 98 per cent decomposes The reaction is therefore reversible $2NH_3 = N_2 + 3H_2$ If water or acid be present, the ammonia is absorbed as fast as it is formed, and the reaction proceeds to an end All the nitrogen and hydrogen combine The two gases nitrogen and hydrogen also combine if heated in the presence of finely divided iron, manganese, uranium, etc The reaction is exothermal $N + 3H = NH_3 + 11\ 4$ Cals The amount of ammonia gas in equilibrium decreases as the temperature rises At 1000° the ammonia is almost completely decomposed. Thus, at atmospheric pressure, and at 30 atmospheres pressure

Temperature	700°	801°	901°	974°	
Ammonia (1 atm)	0 022	0 012	0 007	0 005	per cent per volume
Ammonia (30 atms)	0 654	0 344	0 207	0 15	per cent per volume

The amount of ammonia formed is considerably increased if the pressure be raised. If the gases be kept in circulation so that the ammonia can be removed from the zone of the reaction, F Haber (1906), working at 185 atmospheres pressure, obtained 90 grams of liquid ammonia per hour from a small model apparatus Good results have also been obtained with uranium carbide at 550° as a catalytic agent, and at 750°, and a pressure of 175 atmospheres The process has recently been taken up by the Badische Anilin und Sodafabrik for exploiting commercially, and the use of iron as a catalyst at 600° has been patented

Uses —Ammonia is used in refrigerating machines, as a cleansing agent on account of its property of dissolving greases, in the manufacture of soda by the Solvay process, in chemical operations where a volatile alkali is needed, etc A carboy of ammonia (sp gr 0 88) holds 88–90 lbs The commercial ammonia sells at about *5d* per lb, and the pure at $6\frac{1}{2}d$ per lb

§ 2 The Properties of Ammonia

Ammonia is a colourless gas with a pungent odour If inhaled suddenly, it will bring tears to the eyes, if large quantities be inhaled, suffocation may ensue Ammonia is a little more than half as heavy as air, and consequently, the gas is collected, like hydrogen, by the downward displacement of air

Action of water —The gas is extremely soluble in water one volume of water at 0° and 760 mm dissolves 1298 volumes of gas, and at 20°, 710 volumes The gas can all be removed from its aqueous solution by boiling The great solubility of ammonia in water is illustrated by means of the apparatus indicated in Fig 193, but an ordinary flask will do If a jar of dry ammonia be collected over mercury, and carried on a dish of mercury into a tray of water, and the dish of mercury removed below the surface of water, the absorption of ammonia is so rapid that the cylinder is often broken [1] The specific gravity of the solution of ammonia in water gradually decreases as the concentration of the ammonia increases The freezing curves of mixtures of ammonia and water by

[1] Consequently the hand is protected by holding the cylinder with a piece of cloth

F. F Rupert (1909), Fig 195, show three eutectics and the existence of two hydrates ammonia semihydrate, $2NH_3 H_2O$, which forms small needle like crystals melting at $-79°$, and ammonia monohydrate, NH_3H_2O, corresponding with the so called ammonium hydroxide, NH_4OH. The latter compound forms needle like transparent crystals melting at $-79°$. Solutions of ammonia containing 25 to 60 per cent of ammonia are very viscid at temperatures below $-60°$

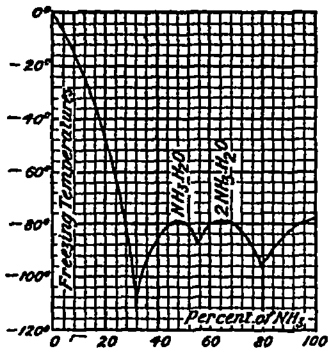


Fig 195 —Freezing Curves of Aqueous Ammonia

Considerable heat is evolved during the solution of the gas $NH_3 + Aq = NH_3aq + 8.4$ Cals. If a rapid current of air be driven through a cold solution of ammonia in water, the heat absorbed as the ammonia is expelled from the solution will reduce the temperature so as to freeze a small globule of mercury The production of cold is best demonstrated by blowing air through a solution of ammonia standing on a few drops of water on a block of wood The beaker will soon be frozen to the block of wood

Refrigeration —The heat of evaporation of liquid ammonia is 5 7 Cals. at $-33°$ This means that 17 grams of liquid ammonia at $-33°$ requires 5 7 Cals of heat before it can pass into a gas at $-33°$ Otherwise expressed, when the gas is liquefied, heat is liberated, and conversely, heat is absorbed when the liquid is vaporized. If, therefore, liquid ammonia be evaporated, a relatively large amount of heat is absorbed from its surroundings Advantage is taken of this fact in the preparation of artificial ice, cold storage, etc Ammonia gas is liquefied by compression in the "condensing coils" by means of a pump, the heat generated as the gas liquefies is conducted away by the cold water flowing over the condensing pipes, Fig 196 The liquid ammonia runs into coils of pipes "expansion coils" dipping in brine The pressure is removed from the liquid ammonia in the expansion coils, and the heat absorbed by the rapidly evaporating liquid cools the brine below zero The gas from the evaporating liquid is pumped back into the condensing coils, and so the process is continuous. Cans of water placed in the brine are frozen into cakes In cold storage rooms, the cold brine circulates in coils near the ceiling of the room to be cooled, and returns to the cooling

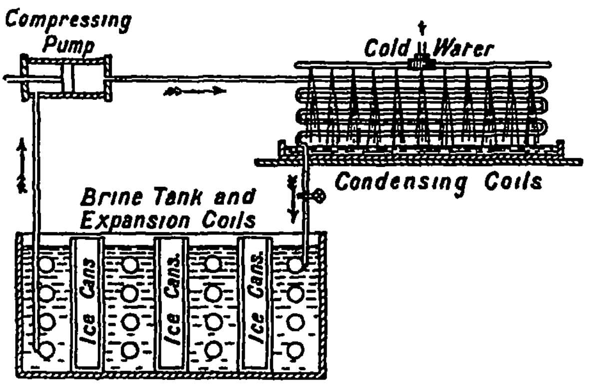


Fig 196 —Refrigeration Plant (Diagrammatic)

tank Sulphur dioxide and carbon dioxide are also employed for refrigeration, but ammonia is more generally used

Double Compounds—Ammonia is absorbed by calcium chloride, zinc chloride, silver chloride, etc, forming double compounds For instance, with silver chloride below 15°, ammonia forms $AgCl\ 3NH_3$, above 20°, $2AgCl\ 3NH_3$, with calcium chloride, $CaCl_2\ 2NH_3$, $CaCl_2\ 4NH_3$; $CaCl_2\ 8NH_3$, and with aluminium chloride, compounds with 1, 3, 5, 6, and 9 molecules of ammonia have been reported

Liquid and solid ammonia—If the compound of silver chloride with ammonia be heated in one leg of a V-shaped hermetically closed tube immersed in water, Fig 100, and the other leg immersed in a freezing mixture—say calcium chloride and ice—the ammonia gas condenses in the cold leg of the V-tube to a colourless limpid liquid Like water, liquid ammonia is a bad conductor of electricity The liquid boils at −33 5°, and solidifies to white transparent crystals at −78°

Oxidation of ammonia—Ammonia is a non-supporter of ordinary combustion and it is incombustible in air It burns in oxygen, forming nitrogen, water, and small quantities of ammonium nitrate, and nitrogen peroxide If ammonia be mixed

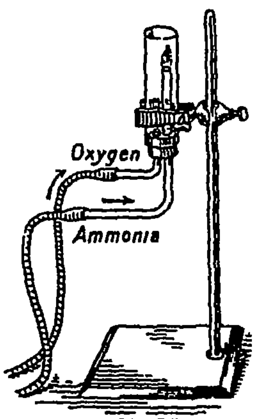


FIG 197—Combustion of Ammonia

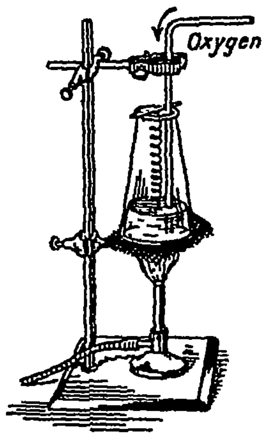


FIG 198—Kraut's Experiment

with oxygen, say, by bubbling a stream of oxygen through a small quantity of concentrated ammonia warmed in a flask, the gas issuing from the flask can be ignited, it burns with a yellow flame In a few moments the solution in the flask will be too dilute to show the flame By sending a jet of ammonia into the air holes of a Bunsen's burner, the flame will be found to expand, and acquire a yellow tinge The effect is shown better by delivering a jet of ammonia into the centre of the tube of a Bunsen's burner If a stream of oxygen be sent into a cylinder fitted as shown in Fig 197, and a stream of ammonia be sent into the same cylinder through a wide glass tube, the ammonia can be ignited, and it will burn with a yellowish flame In K Kraut's experiment (1865), a stream of oxygen is sent through a concentrated solution of ammonia in a beaker in which is suspended a spiral of thin ($\frac{1}{4}$ mm) platinum wire (recently ignited), Fig 198 If the current of oxygen be very slow, the platinum wire will glow red hot, and the beaker will soon be filled with brown fumes of nitrogen peroxide If the current of oxygen be faster, a small explosion will occur every now and again the first explosion will be stronger than the second, the second stronger than the third, etc, and the solution in the beaker will be found to contain both ammonium nitrite and nitrate Here the platinum acts as a catalytic agent (p 132).

If a mixture of ammonia and air be passed through a tube (Fig 190)[1] containing hot platinized asbestos, nitric acid is formed $NH_3 + 2O_2 = H_2O + HNO_3$. A mixture of ammonia and oxygen explodes violently when ignited $4NH_3 + 3O_2 = 2N_2 + 6H_2O$ An aqueous solution of ammonia is oxidized to ammonium nitrite and nitrate and hydrogen peroxide by ozone

Action of ammonia on the metals —When magnesium is heated in ammonia gas, it forms magnesium nitride, Mg_3N_2 As indicated on p 534, the nitrides give ammonia when treated with water Several other nitrides are known, *e.g* Ca_3N_2, AlN, etc When ammonia gas is passed over hot sodium, a compound NH_2Na—sodamide—is formed. Sodamide is made by heating, say, 3 grams of metallic sodium in a deep nickel boat, in a combustion tube, between 300° and 400° in a current of ammonia dried by passing it through a tower of soda lime Hydrogen mixed with the excess of ammonia escapes The reaction is represented $2NH_3 + 2Na = 2NH_2Na + H_2$ The amides of potassium, sodium, etc, are usually decomposed by water forming ammonia, and the hydroxides of the metals

Action of chlorine on ammonia —Chlorine decomposes ammonia gas forming nitrogen (*q v*), and hydrogen chloride. The latter unites with the remaining ammonia forming ammonium chloride If ammonium chloride be treated with an excess of chlorine—say, by inverting a jar of chlorine over a warm (30°–40°) concentrated solution of ammonium chloride—yellow oily drops of nitrogen chloride, NCl_3, are formed The reaction is endothermic $N + 3Cl = NCl_3 - 42$ Cals Nitrogen chloride is one of the most explosive substances known It was discovered by P L Dulong in 1811, who continued to work on it after it had caused him the loss of three fingers and one eye It explodes violently when in contact with many organic substances, exposure to sunlight, and also spontaneously Nitrogen chloride is also formed when a solution of ammonium chloride is electrolyzed, it is also formed when a lump of ammonium chloride is suspended in a concentrated solution of hypochlorous acid, HOCl, and since nitrogen chloride is hydrolyzed by water into ammonia and hypochlorous acid, the reaction $NH_3 + 3HOCl \rightleftharpoons 3HOH + NCl_3$, must be reversible The compound is more stable when it is dissolved in certain solvents, say carbon tetrachloride, CCl_4 Concentrated hydrochloric acid and ammonia both decompose nitrogen chloride forming ammonium chloride and chlorine in the one case, and ammonium chloride and nitrogen in the other Monochloramide—NH_2Cl—is obtained by adding, say, 50 c c of a solution of 3 7 grams of sodium hypochlorite—free from an excess of chlorine—to 100 c c of an aqueous solution containing 0 85 gram of ammonia The liquid ceases to smell of ammonia, and in its place, a penetrating smell of monochloramide, NH_2Cl, is developed $NH_3 + NaOCl = NaOH + NH_2Cl$ Some nitrogen is at the same time evolved owing to the decomposition of the monochloramide $3NH_2Cl = N_2 + NH_4Cl + 2HCl$. The relation of these compounds to ammonia will appear from the graphic formulæ

Ammonia Sodamide Chloramide Nitrogen chloride

[1] The air is driven through a hot solution of ammonia, and then passed over the platinized asbestos

Nitrogen iodide, $N_2H_3I_3$.—The chocolate coloured amorphous powder of nitrogen iodide obtained by the action of aqueous solution of ammonia upon iodine—either solid or in solution—was once thought to be NI_3 analogous with nitrogen chloride, NCl_3. The compound decomposes readily both in diffused daylight, and in the presence of the liquids employed in washing the powder prior to analysis. An exact determination of the composition of the pure substance is therefore difficult, and different results have been obtained with slight variations in the mode of preparation. Many have demonstrated that the compound contains hydrogen; and, in consequence, the formula has been variously given as $N_2H_3I_3$, NH_2I, NHI_2, etc.

Nitrogen iodide is prepared in a state of purity by the action of ammonia upon an aqueous solution of potassium hypoiodite, KIO, in the presence of excess of potassium hydroxide. If the solutions employed be not too concentrated, nitrogen iodide separates in brownish-red crystals with the ultimate composition $N_2H_3I_3$. This may mean that the substance is a compound of nitrogen iodide and ammonia—$H_3N \cdot NI_3$. The reactions just indicated throw some light on the constitution. In the first case, ammonium hypoiodite is probably first formed by the action of ammonia on the solution of iodine: $I_2 + 2NH_4OH = NH_4IO + NH_4I + H_2O$; and with potassium hypoiodite: $KIO + NH_4OH = NH_4IO + KOH$. The unstable hypoiodite spontaneously decomposes producing the compound in question: $3NH_4IO \rightleftharpoons N_2H_3I_3 + NH_4OH + 2H_2O$. This reaction is to some extent reversible, and a small quantity of ammonium hypoiodite is reproduced when nitrogen iodide is suspended in dilute ammonia and exposed to light.

The main action during the decomposition of nitrogen iodide in light is a simple decomposition into nitrogen gas and hydrogen iodide: $N_2H_3I_3 = N_2 + 3HI$. The action is further complicated by the interaction of the hydrogen iodide with the still undecomposed solid. Dry nitrogen iodide exposed to light behaves in a similar manner. Nitrogen iodide is rapidly decomposed by acids and alkalies. Although moist nitrogen iodide can be handled without much danger of explosion, the dry compound is very explosive. Explosions are said to have been produced as a result of the shock of a falling dust-particle, and by a fly walking over the dry powder.

Ammonia as a base.—One of the most striking properties of ammonia chemically speaking is the basic character of its aqueous solution. The aqueous solution turns red litmus blue, yellow tumeric paper brown, conducts electricity, and in general reacts like a base. Indeed it is supposed that a molecule of water combines with a molecule of ammonia to form a solution of ammonium hydroxide: $NH_3 + H_2O = NH_4OH$. Hence aqueous ammonia is sometimes called ammonium hydroxide. If the aqueous solution of ammonia be neutralized with an acid—nitric, sulphuric or hydrochloric acid—the corresponding *ammonium salt* is formed—ammonium nitrate, NH_4NO_3; ammonium sulphate, NH_4HSO_4, or $(NH_4)_2SO_4$; ammonium chloride, NH_4Cl. It will be observed that we are here dealing with a univalent radicle NH_4 which is called ammonium. The assigning of the name does not make this radicle any less hypothetical than if it were nameless. The fact that ammonium appears to form a series of salts closely analogous with the salts of sodium and potassium has instigated many to seek for a compound, NH_4, with a corporeal existence.

The sulphonium bases, SR'_3OH, of organic chemistry are related to hydrogen sulphide, H_2S, similar to the way ammonium hydroxide, NH_4OH, is related to ammonia, NH_3

§ 3 Ammonium Amalgam.

When a little mercury amalgam, *A*, Fig 199, containing about one per cent of sodium or potassium is placed in a solution of ammonium chloride, the mercury swells up into a frothy mass, illustrated in *B*, Fig 199, thirty times its original volume The inflated mass can be compressed or expanded by raising or lowering the pressure If mercury be brought into a concentrated aqueous solution of ammonium, and a current of electricity be passed through the solution in such a way that the cathode dips into mercury (Fig 200), the mercury swells up in a similar manner If the temperature be kept below 0°, the amalgam shows little tendency to inflation

It is supposed that a true solution of ammonium NH_4 in mercury is formed, which rapidly decomposes into mercury, hydrogen, and ammonia when warmed above 0° These gases, entangled with the mercury, are said to cause the frothing Others consider that the amalgam is a mere solution of ammonia and hydrogen in mercury Against this view it is urged that (1) neither of these gases

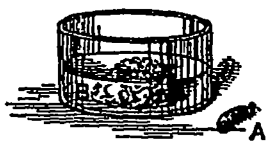


Fig 199—Ammonium Amalgam

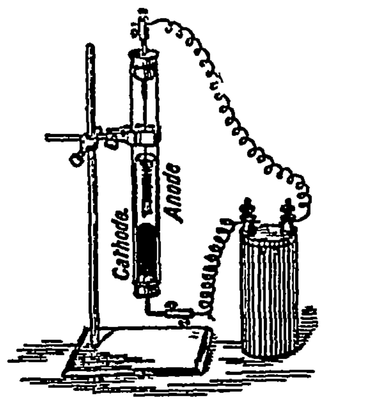


Fig 200—Ammonium Amalgam.

(ammonia or hydrogen) alone or mixed together will dissolve in this manner, (2) the gases bear to one another the ratio $2NH_3 : H_2$, (3) when ammonium amalgam prepared at 0° is brought into contact with cold solutions of copper, cadmium, or zinc sulphate, some of the metal is precipitated and ammonium sulphate is formed it is supposed that $2NH_4 + CuSO_4 = Cu + (NH_4)_2SO_4$ Neither zinc nor cadmium are reduced to the metal by hydrogen or ammonia

§ 4 Ammonium Salts

The ammonium salts are usually very soluble in water, and when the solutions are boiled, partial decomposition occurs The solution, originally neutral, may become acid owing to the volatilization of more ammonia than acid. When the ammonium salts are heated with the fixed alkalies —potassium or sodium or calcium hydroxides, or calcium oxide—the ammonia is volatilized Hence the old term *volatile alkali* for ammonia

Identification of ammonia and ammonium salts.—(1) When the salts are heated with an alkali or lime, the characteristic smell of ammonia is obtained; (2) With hydrochloroplatinic acid, they give a yellow precipitate of ammonium chloroplatinate; (3) Nessler's reagent gives a yellow coloration. The intensity of the tint with a given concentration is nearly proportional to the amount of ammonia present.

Ammonium sulphate.—This salt is usually made from "gas liquor" as indicated on p. 711. It is also formed by the neutralization of ammonia with dilute sulphuric acid. It is used principally as a fertilizer, and also in the manufacture of ammonium compounds.

Ammonium nitrate.—This salt is used chiefly in the preparation of nitrous oxide; and in the manufacture of fireworks and explosives. For instance, the explosive "ammonite" is said to contain between 80 and 90 per cent. of this salt. Four different types of crystals are known, each type has a definite transition temperature. The ordinary crystals are rhombic, and isomorphous with potassium nitrate. The heat of solution is: $2NH_4NO_3 + 400\ Aq = -12.6$ Cals. If 60 parts of the salt be dissolved in 100 parts of water at 13°, the temperature of the liquid falls to about −13°; and if the water be at 0°, the temperature of the liquid falls to about −16°. Hence a mixture of ice and ammonium nitrate is a valuable mixture for reducing the temperature below the freezing point of water. Ice and common salt is often used for the purpose. Such mixtures are called *freezing mixtures* (p. 245).

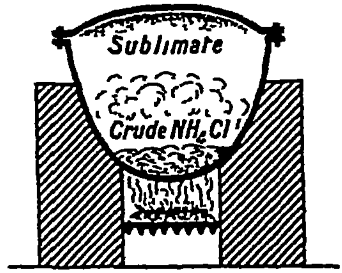


FIG. 201.—Sublimation of Ammonium Chloride.

Ammonium nitrite.—This salt is made by saturating an aqueous solution of ammonia with nitrous acid, or by adding silver nitrite to a solution of ammonium chloride. When heated the solution decomposes into nitrogen and water, so that the crystals cannot be prepared by evaporation in the ordinary manner. The solid can be obtained by evaporating a clear aqueous solution of the salt over sulphuric acid *in vacuo* at ordinary temperatures; or better, by adding ether to an alcoholic solution of the salt when crystals of ammonium nitrite separate. Very little gas is evolved if the salt be heated *in vacuo* below 40°; on cooling most of the salt crystallizes; at 70°, the salt slowly decomposes and a large part sublimes.

Ammonium chloride.—If ammonia gas be brought in contact with hydrogen chloride, dense white fumes of ammonium chloride are formed: $NH_3 + HCl = NH_4Cl$. This can be illustrated by placing a bottle of aqueous ammonia alongside a bottle of hydrochloric acid, and blowing across the mouth of the one bottle to the other. Ammonium chloride is made by mixing an aqueous solution of ammonia and hydrochloric acid, and by passing ammonia gas into dilute hydrochloric acid. The last-named process is usually employed on a manufacturing scale. The crude product is purified by heating the solid in a large iron or earthenware pot with a dome-shaped cover, Fig. 201. The ammonium chloride volatilizes and the solid condenses as a white crystalline fibrous mass inside the cover. Most of the impurities remain in the vessel. The process of

vaporizing a solid and condensing the vapour back to the solid condition is called sublimation. Ammonium chloride is a white granular, fibrous, crystalline solid, with a sharp saline taste. It dissolves in water and at the same time lowers the temperature. The heat of solution is −3.7 Cals. Ammonium chloride is used for charging Leclanché cells; as a constituent of soldering fluids, to protect metals from oxidation during the soldering. It is also used in galvanizing iron, and in the textile industries.

§ 5 The Dissociation of Ammonium Chloride

The vapour density ($H_2 = 2$) of ammonium chloride at 350° is 29.04, and at 1040°, 28.75. The theoretical value for the molecule NH_4Cl is 53.5. Hence we cannot be dealing with that molecule at the temperatures named. Suppose the vapour of ammonium chloride be dissociated so that a mixture of equal volumes of ammonia and hydrogen chloride is formed corresponding with $NH_4Cl = NH_3 + HCl$. The vapour density for complete dissociation would then be 26.75, that is, half the value for NH_4Cl—that is, $\frac{1}{2}$ of (17 + 36.5). The experimental result thus shows that dissociation is nearly

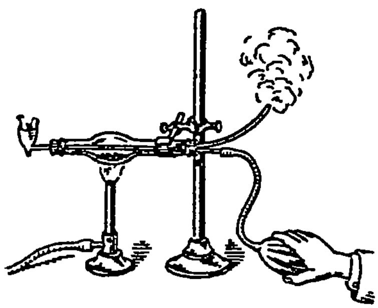


Fig. 202.

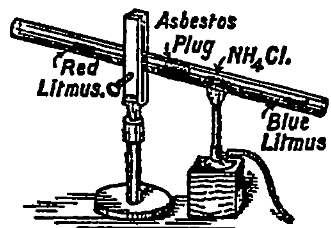


Fig. 203.

Dissociation of Ammonium Chloride.

complete. Applying the method of p. 527, it follows that the vapour contains about 17 per cent. of ammonium chloride, and 83 per cent. of a mixture of equal volumes of ammonia and hydrogen chloride.

According to H. B. Baker (1894), if the vapour density be determined in a vessel of hard glass with a thoroughly dried sample of ammonium chloride, the number is quite normal, namely, 53.4. This shows that the dry salt does not dissociate quickly enough to affect the determination. Obviously, too, the moisture is a catalytic agent which accelerates not only the dissociation, but also the formation of ammonium chloride from ammonia and hydrogen chloride.

The dissociation of ammonium chloride under ordinary conditions is easily illustrated by taking advantage of the difference in the speeds of diffusion of the two gases ammonia and hydrogen chloride. The process of atmolysis (p. 107) can be used. Let the stem of a clay pipe be fixed by corks in a hard glass bulb tube with some solid ammonium chloride in the bulb, as illustrated in Fig. 202. The mouthpiece of the clay pipe is connected with a rubber blower. One cork is fitted with an exit tube. A strip of red and a strip of blue litmus paper are placed in the bowl. When the ammonium chloride has been heated for a short time, blow a

very gentle current of air through the stem of the pipe The red litmus will be coloured blue by the ammonia gas which diffuses through the porous earthenware much faster than the hydrogen chloride The issuing vapour of ammonium chloride reddens blue litmus Another instructive way of showing the same phenomenon is as follows Place a little ammonium chloride near the middle of a piece of hard tube (Fig 203), and a little lower down the tube place a piece of blue litmus paper Place a loose plug of asbestos a little above the salt, and then a piece of red litmus paper Heat the ammonium chloride The ammonia being the lighter gas, diffuses more quickly than the hydrogen chloride Consequently, when the ammonium chloride is heated, the blue litmus will be reddened by the excess of slow diffusing hydrogen chloride in the lower part of the tube, and the red litmus will be blued by the ammonia which passes to the upper part of the tube before the hydrogen chloride

§ 6 The Composition of Ammonia

1 **By explosion with oxygen**—Repeating an old experiment of C L. Berthollet (1785), if ammonia gas be sparked in an apparatus, say, Fig 156, the volume of the gas will be nearly doubled in a short time owing to the dissociation

$$\underbrace{2NH_3}_{\text{2 volumes}} \rightleftharpoons \underbrace{N_2 + 3H_2}_{\text{4 volumes}}$$

As indicated above, about 98 per cent of the gas dissociates in this manner Mix the dissociated gas with sufficient oxygen to give an explosive mixture with the hydrogen, and spark the mixture The contraction will indicate the amount of water in the gas *E g*

Volume of ammonia	10·0 c c
Volume after sparking	19 9 c c
Volume after adding oxygen	72 3 c c
Volume after the explosion	49 9 c c
Contraction	22 4 c c.

The contraction shows that 22 4 c c of water has been formed, two-thirds of this, 14·9 c c, represents the hydrogen obtained from the 10 c c of ammonia used for the experiment Hence 10 c c. of ammonia furnish very nearly 14 9 c c of hydrogen and 5 c.c of nitrogen, that is, three volumes of hydrogen per volume of nitrogen—within the limits of the experimental error

2 **By electrolysis**—If a concentrated aqueous solution of ammonia be electrolyzed (Fig 17), nitrogen and hydrogen are evolved at the two electrodes very nearly in the proportion one volume of nitrogen for three volumes of hydrogen The aqueous ammonia does not conduct very well unless a little ammonium sulphate or other ammonium salt be dissolved in the solution

3 **By A W Hofmann's volumetric method** (*1865*)—In this old experiment, a tube, Fig 204, divided into three equal parts, is filled with chlorine gas, and concentrated aqua ammonia is run through the tap funnel *A*, drop by drop, until the reaction between the chlorine and the ammonia ceases The first drop of ammonia gives a yellowish-green flame, as more ammonia is added, dense clouds of ammonium chloride

are formed, much heat is evolved. Hence it is best to make the experiment with the tube immersed in a cylinder of water When an excess of ammonia has been added, neutralize the excess with dilute sulphuric acid. The gas in the tube was originally at atmospheric pressure, it is now under reduced pressure To restore equilibrium, a long tube is filled with dilute hydrochloric acid, and the long leg allowed to dip in a beaker of dilute hydrochloric acid while the short leg is attached to the funnel as indicated in the diagram, Fig 204 Open the stopcock, and liquid will run into the tube until it reaches the second mark on the tube The tube now contains one volume of nitrogen The interpretation of Hofmann's experiment is as follows The hydrogen of the ammonia and the chlorine combine in equal volumes to form hydrogen chloride The hydrogen chloride combines with the ammonia to form ammonium chloride The tube originally contained three volumes of chlorine This chlorine has taken three volumes of hydrogen to form hydrogen chloride, etc The latter dissolves in the liquid in the tube, and hence is without influence on the volume of the residual nitrogen The three volumes of hydrogen were combined in ammonia with the one volume of nitrogen which remains in the tube This proof is ingenious.

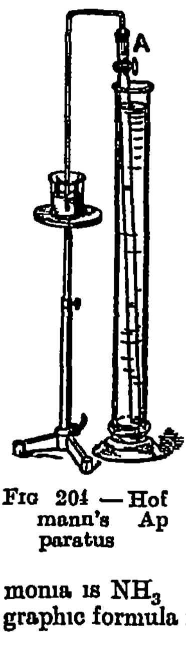


FIG 204 — Hofmann's Apparatus

4 **The vapour density of ammonia and Avogadro's hypothesis** —The three proofs just considered[1] show that three volumes of hydrogen combine with one volume of nitrogen to form ammonia. By Avogadro's hypothesis, the number of molecules which combine are in the same ratio, and since the two gases hydrogen and nitrogen have diatomic molecules, it follows that ammonia contains three atoms of hydrogen for one atom of nitrogen Hence the formula of ammonia must be NH_3, or N_2H_6, etc The vapour density of ammonia ($H_2 = 2$) is nearly 17 If the atomic weight of hydrogen be 1 and nitrogen 14, the molecular weight of ammonia is 17 This agrees with the number obtained for the vapour density Hence the formula of ammonia is NH_3 Here the nitrogen atom is tervalent, and accordingly the graphic formula for ammonia is

$$\begin{matrix}H\\H\end{matrix}\!\!>N-H$$

5 **Gravimetric analysis** —The composition of ammonia by weight can be verified by gravimetric analysis. Ammonia gas is passed over a tube containing heated copper oxide The resulting water is weighed—Fig 14 —and the volume of nitrogen passing along is determined, and the corresponding weight computed (p 67) The numbers so obtained give the combining proportions of hydrogen and nitrogen in ammonia. The result shows that 14·01 parts of nitrogen are combined with 3 024 parts of hydrogen. The molecular formula is then to be established by Avogadro's hypothesis

[1] Others are available if needed

§ 7 Molecular Compounds and Compound Salts

The eye may rest with complacency upon the simple beauty of the law which governs the construction of bodies belonging to the type of ammonia —A W HOFMANN

It seems as if tervalent nitrogen in ammonia, NH_3, changes into quinquevalent nitrogen in forming ammonium chloride, NH_4Cl But the ready dissociation of ammonium chloride into ammonia and hydrogen chloride led A Kekulé (1864) to assume the existence of what he designated "molecular compounds" Kekulé applied the term "atomic compounds" to those compounds in which all the atoms of the elements are united in such a way that their valencies are saturated "These," said Kekulé, "are the true chemical molecules, and the only ones which can exist in the gaseous state" He assumed that the atoms of different molecules could attract one another so as to produce a kind of coupling of the molecules The nature of the atoms of the copulated molecules may be such that double decomposition is not possible, and "the two molecules, so to speak, adhere and form a group endowed with a certain amount of stability, which is always less than that of atomic combination" In other words, Kekulé assumed that molecular compounds are formed by direct addition of two or more simple molecules, and the simple molecules retain to some extent their individuality, for they can be readily separated from one another apparently unchanged Kekulé cited as examples of molecular compounds ammonium salts, phosphorus pentachloride, iodine trichloride, crystalline salts which furnish anhydrous salt and water, etc The compounds of silver chloride and ammonia, ferrous sulphate and nitric oxide, etc, can be added to the list To sum up Kekulé's position in order to make the theory of constant valency compatible with the existence of more complex molecules, it was assumed that these "molecular compounds" belonged to a different type of combination The question is not so easily answered

If phosphorus in phosphorus trifluoride, PF_3, be tervalent, phosphorus pentafluoride, PF_5, must, according to Kekulé, be a molecular compound of PF_3 and F_2, and, as such, PF_5 should be unstable and break down into its two atomic constituents when heated According to T E Thorpe (1876), phosphorus pentafluoride is a gas stable at high temperatures Hence the valency of an element depends on the number of atoms with which it is associated, or else the molecular compound is more stable than Kekulé supposed

V Meyer and Lecco (1874) applied an ingenious experiment to test whether nitrogen be ter- or quinquevalent in the ammonium salts. It is undoubtedly tervalent in ammonia, NH_3 Meyer and Lecco's argument will appear from the following considerations In organic chemistry, a series of compounds is discussed in which the hydrogen atoms of ammonia are replaced, one by one, with equivalent univalent radicles—methyl, CH_3, ethyl, C_2H_5, —to form a series of compounds called the amines or substituted ammonias in which nitrogen is undoubtedly tervalent Thus

$\begin{matrix}H\\H\end{matrix}\!>\!N—H$	$\begin{matrix}CH_3\\H\end{matrix}\!>\!N—H$	$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!N—H$	$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!N—CH_3$	$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!N—C_2H_5$
Ammonia	Methylamine	Dimethylamine	Trimethylamine	Dimethylethylamine

Like ammonia, (1) the amines combine directly with acids to form compounds resembling the ammonium salts, e g trimethylamine unites directly with hydrogen chloride to form trimethylammonium chloride $N(CH_3)_3 + HCl = NH(CH_3)_3Cl$, and (2) the amines combine with methyl or ethyl iodides, etc, to form corresponding compounds E g trimethylamine unites with ethyl iodide $N(CH_3)_3 + C_2H_5I = N(CH_3)_3C_2H_5I$ The properties of the compound $N(CH_3)_3C_2H_5I$ formed by the union of $N(CH_3)_3$ with C_2H_5I are identical with the compound $N(CH_3)_2C_2H_5 CH_3I$ formed by the union of $N(CH_3)_2C_2H_5$ with CH_3I Consequently, the two compounds must have the same constitution And it is inferred that the **ammonium salts cannot be molecular compounds as postulated by Kekule and that the nitrogen in ammonium compounds is not tervalent but rather quinquevalent.** This is virtually Ampère's ammonium theory propounded in 1815 The argument is not quite sound, because it is possible that the groups are rearranged during the formation of the compounds by the different processes, so that the most stable configuration is always formed, and one final product is obtained by the two different reactions This subject will be resumed when discussing Werner's theory

Two or more simple salts, as we have seen, each primarily formed by the union of base and acid, may unite to form other salts—**compound salts** of greater complexity, sometimes called molecular compounds The compound salts are often well crystallized, and they are frequently formed by replacing one or more molecules of the water of crystallization by equivalent molecules of another salt. There are three types indicated in what precedes

1 **Mixed crystals and solid solutions** —Potassium perchlorate and potassium permanganate are isomorphous, and form mixed crystals of all shades of colour ranging from a faint pink to a deep purple according to the relative proportions of the two salts in the crystals The physical properties of the mixed crystals are additive, that is, continuous functions of their compositions, and aqueous solutions of the mixed crystals give reactions characteristic of their components—in the present example, of potassium perchlorate and permanganate The two salts form crystals containing all possible proportions between 100 per cent potassium perchlorate and 100 per cent potassium permanganate, as discussed under Retger's law (*q v*)

2 **Double salts** —As in the case of mixed crystals, aqueous solutions of double salts give reactions characteristic of the component simple salts, but the physical properties of the solid salt are not necessarily additive, and the component salts only unite in simple molecular ratios. For instance, lithium chloride, LiCl, and green cupric chloride, $CuCl_2.2H_2O$, unite to form ruby-red crystals, and an aqueous solution gives reactions characteristic of chlorides, copper, and lithium It is pure chance if the composition of a mixed crystal happens to be in simple molecular ratio since a variation in composition of the mother liquid from which the crystals are deposited will be attended by a variation in the composition of the crystals A change in the composition of the liquid may change the composition of the compound salt, but the change will be abrupt, not gradual, in harmony with the law of multiple proportions.

3 **Complex salts or salts of complex acids** As in the case of double salts, the component simple salts of the so called complex salts are

combined in a simple molecular ratio, and the resulting compound salt is quite distinct from a mechanical mixture of the component salts, and unlike double salts, the chemical properties of a solution of a complex salt are different from the properties of solutions of the component salts The term "double salt" is often applied somewhat loosely to compound salts formed by the union of one or more molecules of one salt with one or more molecules of another salt, but, as W Ostwald said in 1889, the term "double salt" should not be applied to combinations of two salts which give reactions different from those of the constituent salts For example, the complex salt potassium ferrocyanide is a compound salt formed by the reaction $4KCy + FeCy_2 = K_4FeCy_6$ The product of this combination does not give the analytical reactions characteristic of potassium cyanide nor of ferrous cyanide In the language of the ion theory, this is expressed by saying that the ions of complex salts in solution are different, and the ions of double salts are similar to the ions of the simple salts from which they are derived The ions of potassium cyanide (neglecting secondary reactions) are K and Cy′, and the ions of ferrous cyanide, Fe and Cy′ The ions of potassium ferrocyanide, on the contrary, are K and $FeCy_6''''$ There are, therefore, no ions of Cy′ and of Fe in an aqueous solution of potassium ferrocyanide

The physical properties of a double salt in solution may or may not be different from those of a simple mixture of the constituents In the limiting case, the physical properties will be additively those of their components, but in some cases, this is not the case For *instance*, the solid double salt $FeCl_3$ 2KCl.H_2O is red A concentrated aqueous solution of the double salt, or of an equivalent mixture of the component salts, at 15° has the characteristic yellow tint of ferric chloride, $FeCl_3$, but at about 30° the yellow colour gives way to red. This is supposed to show that the double salt is not dissociated into its constituent molecules at 30°, but it is dissociated at 15° Ferric chloride alone in solution does not give the red colour at 30° Similar remarks apply to many other physical properties of double salts A complex salt might dissociate under certain conditions of temperature so that it acts as a double salt at one temperature, and as a complex salt at another

§ 8 Hydroxylamine

Molecular weight, NH_3O = 33 03 Melting point, 33 05°, decomposes when heated at ordinary pressures but boils at 58° under a pressure of 22 mm

The preparation of hydroxylamine hydrochloride—Hydroxylmaine is formed by the reduction of nitric oxide, nitric acid, or certain nitrates For instance, a stream of nitric oxide may be passed through a solution of tin dissolving in hydrochloric acid $2NO + 3H_2 = 2NH_3O$ The solution will contain a compound of hydroxylamine and hydrogen chloride —hydroxylamine hydrochloride—and also tin chloride The tin may be precipitated by passing hydrogen sulphide through the solution The liquid is then filtered and evaporated to dryness Digest the residue with absolute alcohol On evaporating the solution, white *crystals* of hydroxylamine hydrochloride, NH_3O HCl, are obtained *Hydroxylamine* hydrochloride is now largely made by the electrolytic reduction of nitric acid. E. Divers and T Haga's process (1896), in *which* sulphur dioxide is passed *into* a solution containing equimolecular proportions of sodium carbonate and nitrate, is a more easily conducted process with a good yield.

The preparation of hydroxylamine.—To isolate hydroxylamine, dissolve the hydrochloride in methyl alcohol and add sodium methylate

(obtained by dissolving metallic sodium in methyl alcohol). Sodium chloride is precipitated in the alcoholic solution. Filter off the sodium chloride, and remove the alcohol by distillation—at first under ordinary pressure and then under reduced pressure (p. 104). The hydroxylamine distils at about 70° under a pressure of 60 mm., or at, say, 58° under a pressure of 22 mm.

Properties.—Hydroxylamine crystallizes in the form of white needle-like crystals without smell. The crystals melt at 33°, and boil at 58° under a pressure of 22 mm. At ordinary pressures hydroxylamine gradually decomposes if heated, over 15°, and at higher temperatures it is liable to decompose explosively with a yellow flash. Hydroxylamine resembles ammonia in many respects—it dissolves in water forming a strongly alkaline solution; it reacts with acids forming salts—$NH_3O.HCl$; $(NH_3O)_2.H_2SO_4$; $NH_3O.HNO_3$, etc. The salts all decompose more or less violently when heated. The nitrate furnishes nitric oxide and water, and the nitrite furnishes nitrous oxide and water. Compounds like NH_2ONa and $(NH_2O)_2Ca$ are known as **hydroxylamates**. Hydroxylamine thus behaves towards alkalies like a weak acid and towards acids like a weak base, *i.e.* hydroxylamine behaves as if it were both an acid as well as a base.

Hydroxylamine salts are used as reducing agents in analytical work. Hydroxylamine precipitates metallic silver from silver nitrate; it reduces mercuric chloride to mercurous chloride; it precipitates cuprous oxide from cupric salts; chromium hydroxide from chromic salts, etc. It oxidizes greenish ferrous hydroxide suspended in an alkaline solution to red ferric hydroxide, and at the same time ammonia is formed. If the precipitate be dissolved in an acid, and treated with hydroxylamine, the solution becomes colourless owing to the reduction of the red ferric to greenish ferrous salt. See p. 554.

Composition.—The molecular weight by the freezing point process corresponds with NH_3O. It is generally supposed that hydroxylamine has a similar constitution to ammonia, but one hydrogen atom of the ammonia is replaced by hydroxyl:

$$\begin{matrix}H\\H\end{matrix}\!>\!N{-}H \qquad \begin{matrix}H\\H\end{matrix}\!>\!N{-}OH, \text{ or} \qquad \begin{matrix}H\diagdown\\H{-}\\H\diagup\end{matrix}\!N{=}O$$

Ammonia. Hydroxylamine Hydroxylamine

Hence the alternative term "oxyammonia" for hydroxylamine. Some consider that the graphic formula should be written $H_3{\equiv}N{=}O$, but the compound seems to exhibit a kind of desmotropism, forming what are called **oxonium salts** when it acts as a base (oxygen quadrivalent), and hydroxylamates when it acts as an acid:

$$\begin{matrix}H\diagdown\\H{-}\\H\diagup\end{matrix}\!N{=}O\!<\!\begin{matrix}H\\NO_3\end{matrix} \qquad \begin{matrix}H\\H\end{matrix}\!>\!N{-}O{-}Na$$

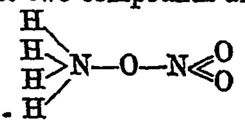
Hydroxylamine nitrate Sodium hydroxylamate

History.—Hydroxylamine salts, and the aqueous solution of the base, were first prepared by W. Lossen (1865), and anhydrous hydroxylamine was simultaneously made by different processes by L. de Bruyn and by L. Crismer in 1890–91.

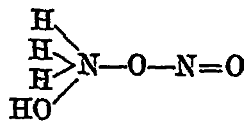
§ 9 Isomerism

The great interest of isomerism has been to introduce into science the principle that substances may be, and are, essentially different solely because the arrangement of the atoms in their chemical molecules is not the same —L PASTEUR

It was once thought to be self-evident "that substances which contain the same atoms and the same relative quantities of these must of necessity have the same chemical properties", we now believe that the atoms of a molecule are arranged according to plan so definite and precise, that two different atoms cannot change places without altering the properties of the substance This does not mean that the relations of the atoms for one another are necessarily immovable, for, as indicated on p 121, the atoms may revolve about a position of equilibrium without altering their order of succession Ammonium nitrate and hydroxylamine nitrite are two different substances with the same ultimate composition, the same molecular weight, and both furnish nitrous oxide and water when heated. There the similarity almost ends The general properties of the two salts are so very different, that there is little room for doubt that the constitution of the molecules must be quite different. The probable constitutional formulæ of the two compounds are



Ammonium nitrate



Hydroxylamine nitrite

We have met several compounds which have the same ultimate composition, but a different molecular weight, and different properties *E g* NO_2 and N_2O_4, the α- and β sulphur trioxides, etc It is convenient to fix these ideas definitely by the use of the special term isomerism—from the Greek ἴσος (isos), the same, μέρος (meros), part Isomerism is a general term applied when the percentage composition of two or more substances is the same, but the properties are different The term "allotropism" is reserved for the special case of isomerism among elements, p 403, and "isomerism" for compounds Polymerism is applied when the percentage composition of two or more substances is the same, but the molecular weight is different, p 402 It is *supposed* that in most cases allotropism is a special case of polymerism Metamerism—from the Greek μετά (meta), change—is applied when the percentage composition and molecular weights are the same, but the properties are different—*e g* hydroxylamine nitrite and ammonium nitrate Desmotropism or tautomerism, p 425, and physical, geometrical or enantiomorphic isomerism—the stereoisomerism of the tartaric acids—discussed on p 516, are special cases of metamerism To summarize [1]

Same ultimate composition, properties different:

I Elements	ALLOTROPISM
II Compounds	ISOMERISM
(1) Molecular weights different	POLYMERISM
(2) Molecular weights the same	METAMERISM
(a) Relative positions of some radicles labile, not fixed	DESMOTROPISM
(b) Certain radicles are enantiomorphic	GEOMETRICAL ISOMERISM

[1] In different text-books there is some difference as to the exact meaning assigned to the different terms here summarized There are also other peculiarities not covered by the terms in the text.

§ 10 Hydrazine or Diamide

Molecular weight, $N_2H_4 = 32.05$ Melting point, 1.4°, boiling point 113.5°, critical temperature, 380°

The preparation of hydrazine sulphate.—The most convenient methods of preparing hydrazine are described in text-books of organic chemistry, but it may be obtained quite as conveniently from purely inorganic substances Mix 200 c.c. of a 20 per cent solution of ammonia, 5 c.c. of a one per cent solution of glue or gelatine,[1] and 100 c.c. of an acqueous solution of 7.5 grams of sodium hypochlorite—free from an excess of chlorine—in a litre flask Boil the mixture for about half an hour when it will have evaporated to about half its original volume Monochloramide is first formed (p. 538), and this reacts with another molecule of ammonia to form hydrazine hydrochloride $NH_2Cl + NH_3 = N_2H_4.HCl$ When cold, place the flask in iced water, and add 20 c.c. of a solution containing 1.96 gram of sulphuric acid, H_2SO_4 Hydrazine sulphate crystallizes out This may be purified by recrystallization from water The process is used technically for the preparation of hydrazine sulphate

The preparation of hydrazine hydrate and hydrazine.—When hydrazine sulphate is distilled with potassium hydroxide in a silver vessel, screwed at the junctions, hydrazine hydrate is obtained $N_2H_4.H_2SO_4 + 2KOH = N_2H_4.H_2O + K_2SO_4 + H_2O$ The free base hydrazine is made by adding small quantities of the hydrate to barium oxide in a glass flask cooled in a freezing mixture The mixture is then distilled under reduced pressure. The barium oxide removes the water from the hydrate $BaO + N_2H_4.H_2O = Ba(OH)_2 + N_2H_4$ F Raschig's method of distilling with sodium hydroxide gives a better yield.

Properties.—Hydrazine hydrate is a colourless fuming corrosive liquid soluble in water It boils at 118°, and freezes to a white crystalline solid melting at 40° It attacks glass, cork, and rubber It is strongly basic, and forms a series of salts with the acids, *e.g.* hydrazine monochloride, $N_2H_4.HCl$, and hydrazine dichloride, $N_2H_4.2HCl$ Hence hydrazine is a diacid base Most of the salts are very soluble in water The sulphate, $N_2H_4.H_2SO_4$, is not so soluble Hydrazine and its salts are among the most powerful reducing agents known, they reduce cupric salts to red cuprous oxide, and precipitate metallic silver from silver nitrate, mercury from mercuric chloride, etc

The free base is a colourless, fuming liquid boiling at 56° under a pressure of 71 mm., and at 113.5° under a pressure of 761 mm The liquid freezes at 0°, and melts at 1.4° When heated to about 350° it decomposes into ammonia and nitrogen $3N_2H_4 = N_2 + 4NH_3$ Hydrazine is slowly oxidized in air with the liberation of free nitrogen, and it burns with a violet-coloured flame.

Composition.—The vapour density of the hydrate at 100° is 50 This corresponds with the molecule $N_2H_4.H_2O$ The hydrate dissociates into water and free base *in vacuo* at 100°, and at 143° dissociation is complete At 183°, under atmospheric pressure, the hydrate decomposes into nitrogen and ammonia. A freezing point determination of the aqueous solution

[1] The action of the gelatine is not understood The glue and gelatine are not necessary, but the yield of hydrazine is much reduced if the mucilage be absent This is an empirical fact It is generally stated that gelatine prevents the formation of nitrogen chloride

gives a molecular weight corresponding with the dihydrate, $N_2H_4 . 2H_2O$. The constitution of the hydrate is either

$$NH_2—NH_3—OH, \text{ or } \begin{matrix} H_3N \\ H_3N \end{matrix}\!\!>O$$

History.—Hydrazine hydrate was discovered by T. Curtius in 1887, and the base was isolated by L. de Bruyn, 1895. The substitution products —e.g. phenylhydrazine, $C_6H_5 . HN . NH_2$—have been known for a longer time. E. Fischer made the first organic derivative in 1875.

§ 11. Hydrazoic Acid, Hydronitric Acid, or Azoimide

Molecular weight, $N_3H = 43.04$. Melting point, $-80°$; boiling point, $37°$.

The successful attempt to double ammonia on itself, resulting in the discovery of hydrazine, was followed by a further attempt to replace another hydrogen atom by a NH_2 group, and so form triamine or triazine $H_2N . NH . NH_2$; but this could not be accomplished, for the terminal hydrogen atoms dropped out and a closed ring of three nitrogen atoms, N_3H, was the result.

Preparation.—Like hydrazine, this compound is best made by organic processes. Hydrazoic acid was discovered by T. Curtius (1890). W. Wislicenus (1892) made it from inorganic materials by passing dry ammonia over metallic sodium in a nickel boat in a tube between 250° and 350° so as to make sodamide: $2Na + 2NH_3 = 2NaNH_2 + H_2$. When all the sodium has been converted into the amide (about six hours), the current of ammonia is replaced by a stream of dry nitrous oxide, and continued at 190° until ammonia is no longer evolved (about five hours):

$$\begin{matrix} N \\ N \end{matrix}\!\!>O + \begin{matrix} H \\ H \end{matrix}\!\!>N—Na = H_2O + \begin{matrix} N \\ N \end{matrix}\!\!>N—Na$$

The product of the action—a mixture of NaOH and NaN_3—is dissolved in water; the solution acidified with dilute sulphuric acid (1 : 1); and distilled. The first quarter of the distillate contains most of the hydrazoic acid. Hydrazoic acid can also be made by treating nitrogen chloride, NCl_3, or an aqueous solution of silver nitrite with hydrazine sulphate. In the latter case a crystalline precipitate of silver hydrazoate, N_3Ag, is formed in a short time—A. Angeli (1893). The reaction may be symbolized:

$$\begin{matrix} NH_2 \\ NH.HCl \end{matrix} + NO.OH = \begin{matrix} N \\ N \end{matrix}\!\!>N.H + 2H_2O + HCl$$

The preparation of hydrazoic acid by the action of nitrous acid on salts of hydrazine resembles a well known method of preparing nitrogen from ammonium salts by the action of nitrous acid—say by heating ammonium chloride with sodium nitrite—writing nitrous acid in place of the latter:

$$\begin{matrix} NH_2 \\ H_2.HCl \end{matrix} + NO.OH = \begin{matrix} N \\ N \end{matrix} + 2H_2O + HCl$$

The aqueous solution of the free acid can be obtained by distillation with sulphuric acid as indicated above; repeated fractional distillation furnishes a solution containing 91 per cent. of hydrazoic acid. The remaining water must be removed by calcium chloride.

Properties.—Pure hydrazoic acid is a colourless mobile liquid, with an unpleasant penetrating odour. It boils at 37°; it can be solidified by cooling. The solid melts at $-80°$. Work with hydrazoic acid and its

salts is dangerous because these compounds are rather unstable, and very liable to explode The acid is partly reduced by sodium amalgam, forming ammonia and a little hydrazine $N_3H + 3H_2 = N_2H_4 + NH_3$ Potassium permanganate oxidizes it to water and nitrogen, oxygen is also liberated at the same time Ferric salts give a deep red coloration

The acid is soluble in water The aqueous solution behaves as a strong monobasic acid, and it readily dissolves zinc, iron, cadmium, magnesium, and aluminium with the evolution of hydrogen and ammonia, and the formation of salts—called hydrazoates, or azides, or trinitrides It also gives insoluble silver and mercury salts, AgN_3 and HgN_3, both of which are very explosive Leadazide, PbN_6, is used as a detonator in place of mercury fulminate for trinitrotoluol, it is considered less sensitive and safer The salts are usually anhydrous and crystalline, and when heated give the pure metal The aqueous solution and the alkaline salts are not so liable to explode as the salts of the heavy metals With ammonia, hydrazoic acid forms the ammonium salt $NH_3 HN_3$, or $NH_4 N_3$, that is, N_4H_4, and with hydrazine, $N_2H_4 HN_3$, that is N_5H_5 With sodium hypochlorite and acetic acid, hydrazoic acid furnishes a colourless highly explosive compound, chlorazide, N_3Cl, which smells like hypochlorous acid Silver azide with a cold ethereal solution of iodine, furnishes a yellow explosive compound iodozide, N_3I

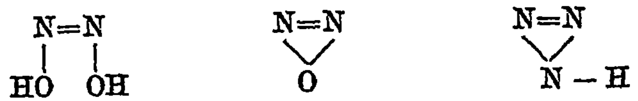
Constitution —On electrolysis, hydrazoic acid yields rather less than three volumes of nitrogen per one volume of hydrogen The low yield of nitrogen is due to secondary reactions Analyses and vapour density determinations agree with the formula N_3H. The formation of hydrazoic acid from sodamide and nitrous oxide, and also by the action of hydrogen on thallium trinitride, which results in the formation of nitrogen and ammonia, agrees with the structural formula —

$$\mathrm{H{-}N{<}}\begin{matrix}\mathrm{N}\\ \mathrm{N}\end{matrix}$$

With metals below magnesium in the electrochemical series, Table XXIII, hydrazoic acid is reduced to ammonia, and may be to hydrazine and free nitrogen, no hydrogen is evolved, *e g* $Cu + 3HN_3 = CuN_6 + N_2 + NH_3$, with nitric acid, it will be remembered that $3Cu + 8NHO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$ With some of the oxidizable non metals, the acid is reduced, forming ammonia and nitrogen, thus, $H_2S + HN_3 = S + N_2 + NH_3$, with nitric acid, we have $3H_2S + 2HNO_3 = 3S + 2NO + 4H_2O$ With metals lying near the end of the electrochemical series, the acid is reduced, forming ammonia and nitrogen, $Pt + 2HN_3 + 4HCl = PtCl_4 + 2N_2 + 2H_3N$, with nitric acid under similar conditions, $3Pt + 4HNO_3 + 12HCl = 3PtCl_4 + 4NO + 8H_2O$

Assuming that if two compounds behave in a similar manner they have an analogous structure, it follows if nitric acid has the structure $\mathrm{H{-}O{-}N}{\lessgtr}\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}$ with a pentavalent nitrogen atom as a nucleus united with oxygen, then in hydrazoic acid we can expect a pentavalent nitrogen united with nitrogen, or $H{-}N{=}N{\equiv}N$ (J W Turrentine, 1912), hence the alternative term, "hydronitric acid," for this compound. The latter formula also agrees with some reactions studied in organic chemistry (Thiele, 1911)

The following graphic formulæ show the relations between hydrazoic acid, nitrous oxide, and hyponitrous acid



Hyponitrous acid — Nitrous oxide — Hydrazoic acid.

There are many resemblances between this acid and hydrochloric acid, which suggests that the triazo-group, N_3, in its chemical properties bears a strong family resemblance to the halogens

Nitrogen gas is rivalled only by argon and its congeners in its reluctance to take part in chemical changes, but when united with other elements it leads to forms of activity in great profusion, so much so that M O Forster (1911) styled nitrogen the most versatile form of elemental matter, for union with different proportions of hydrogen furnishes three highly active substances—ammonia, hydrazine, and hydrazoic acid—which have characteristics which stand in marked contrast with one another If oxygen be brought into the system, hydroxylamine, nitrous acid, and nitric acid may be mentioned as typical materials capable of entering into chemical changes of the most diverse order Enumerating the nitrogen-hydrogen compounds

Basic			Acidic	
NH_3	N_2H_4	N_5H_5	N_3H	N_4H_4
Ammonia	Diamide or hydrazine	Hydrazine azoimide	Azoimide or hydrazoic acid	Ammonium azoimide

To these can be added hydrazine hydrazoate, N_5H_5, and possibly also basic ammonium, NH_4, and *diimide*, N_2H_2, which is said to have been made by heating ammonium chloroplatinate $(NH_4)_2PtCl_6 = Pt + 6HCl + N_2H_2$, but there is some doubt if this is really the case

Questions

1 Calculate the vapour density of ammonium chloride By experiment it is found to be 13 345 How do you explain the difference between the calculated and the observed results ? Can you give any experimental evidence in support of your explanation ? Do you know of any other similar cases ?—*Science and Art Dept*

2 Calculate the weight of nitrogen contained in one cwt of (*a*) ammonium sulphate, (*b*) sodium nitrate Describe exactly how you would distinguish these two substances when mixed together in solution —*Aberdeen Univ*

3 How would you prepare in the laboratory a vessel full of ammonia ? Describe experiments by which you could demonstrate that ammonia (*a*) is very soluble in water, (*b*) combines with acids to form salts, (*c*) contains hydrogen —*Victoria Univ, Manchester*

4 What is the action of ammonia gas on (*a*) hot copper oxide, (*b*) hydrochloric acid, (*c*) chlorine water ?—*St Andrews Univ*

5 Why are the compounds formed by the union of acids with ammonia termed ammonium compounds ? Quote facts which may be regarded as evidence that a solution of ammonia in water contains ammonium hydroxide —*London Univ*

6 What are the two main sources of supply of inorganic nitrogen compounds ? Outline three methods which have been suggested for the production of ammonia from atmospheric nitrogen —*Sheffield Univ*

7 How can it be shown that the vapour obtained by heating slightly moist ammonium chloride consists of a mixture of ammonia and hydrogen chloride gases ? What is the density relative to hydrogen of the vapour given off by ammonium chloride, and what would be the density if the vapour consisted of

ammonium chloride ? ($N = 14$, $Cl = 35.5$) Mention other decompositions of a similar nature with which you are acquainted —*Univ North Wales*

8 Give the volume relations between the gases in the following reactions: Hydrogen and chlorine combining to form hydrochloric acid, hydrogen and oxygen combining to form steam, hydrogen and nitrogen combining to form ammonia If a million molecules of hydrogen took part in each reaction, how many molecules of each product would be formed ?—*Sheffield Scientific School, U S A*

9 Explain why the formula of ammonia gas is given as NH_3 and give an account of any theories involved in your answer —*Aberystwyth Univ*

10 Define the terms "acid," "base," "acid salt," "basic salt," "double salt," "complex salt," and supply one illustration of each —*Sheffield Univ*

11 What is hydroxylamine ? Describe and explain the process by which the hydrochloride is prepared from potassium nitrite What is its action upon a solution of a cupric salt, and to what useful purpose has hydroxylamine been applied ?—*Science and Art Dept*

12 What is the effect of passing chlorine gas through aqueous solutions of (*a*) ammonia, (*b*) sulphur dioxide (*c*) ferrous sulphate ? What is the effect of passing sulphur dioxide gas through (*a*) aqueous solutions of potassium permanganate (*b*) concentrated nitric acid ? Give equations —*St Andrews Univ*

13 How is ammonia gas prepared pure and dry ? Give the names and formulæ of the compounds derived from ammonia by replacing one or more of its atoms of hydrogen by (*a*) hydroxyl (*b*) chlorine, (*c*) methyl Describe the preparation and properties of any *two* of these compounds —*London Univ*

14 What change takes place when chlorine is passed into a solution of ammonia ? How can the experiment be conducted so as to afford evidence of the constitution of ammonia ?—*Board of Educ*

15 How is the so-called ammonium amalgam prepared ? Describe its principal properties and explain the various views which have been held as to its nature —*Board of Educ*

16 By what means has the relative rate of diffusion of gases been determined ? Describe an experiment by which you might test whether a gas was dissociated at a high temperature into simpler constituents Two vessels *A* and *B* containing respectively chlorine, and a mixture of an inert gas with 10 per cent of oxygen, were put into communication through a small hole After diffusion had taken place for a short time, the chlorine in *A* was absorbed by potash, and the residual gas in *A* was found to contain 11 per cent of oxygen What was the density, approximately, of the inert gas ?—*Victoria Univ, Manchester*

Note for Page 548

If a solution of hydroxylamine and sodium hydroxide in methyl alcohol be treated with methyl nitrate, CH_3NO_3, a white powder is precipitated It has the empirical composition $Na_2N_2O_3$ This substance appears to be the sodium salt of a very unstable acid—nitrohydroxylamic acid, $H_2N_2O_3$—for if the salt be treated with a mineral acid, the product which is liberated begins at once to decompose with brisk effervescence, forming nitric oxide and water $H_2N_2O_3 \rightarrow 2NO + H_2O$ The acid thus appears to be a *hydrate of nitric oxide.* In addition to the sodium salt, some organic derivatives have been made The constitutional formula is usually written $HO-N=NO-OH$ The sodium salt rapidly absorbs oxygen from the air forming sodium nitrite and nitrate, and when the solution is boiled it furnishes sodium nitrite, etc, as symbolized in the equation $2Na_2N_2O_3 + H_2O \rightarrow 2NaNO_2 + N_2O + 2NaOH$, the heating of the solid salt furnishes sodium nitrite and hyponitrite $2Na_2N_2O_3 = 2NaNO_2 + Na_2N_2O_2$ The acid and its salts are interesting in that they may decompose in at least six different ways, as symbolized

$$2H_2N_2O_3 \begin{cases} = 4NO + 2H_2O \\ = 2HNO_2 + H_2N_2O_2 \\ = 2HNO_2 + 2NO + H_2 \\ + 2H_2O = 2NH_2OH + 2HNO_2 + O_2 \\ = 2NO_2 + H_2N_2O_2 \\ = 2HNO_2 + N_2O + H_2O \end{cases}$$

CHAPTER XXIX

Nitrogen and Atmospheric Air

§ 1 Nitrogen—Occurrence and Preparation

Atomic weight, N = 14 01, molecular weight, N_2 = 28 02 Bi-, ter-, and quinque-valent Melting point, −210 5°, boiling point −195 5°, critical temperature −146° Relative vapour density (H_2 = 2), 27 81, (air = 1) 0·967 One litre under normal conditions weighs 1 2506 grams

History —It is difficult to state precisely who first isolated nitrogen and clearly recognized it as a definite substance John Mayow (1674) and several others got very near, if they did not get actually there The man who deduces on good mental evidence, or even proves by actual experiment, the existence of something not known before is not always recognized as the discoverer, but rather is he hailed discoverer who proves by a conclusive series of experiments that the substance in question has properties distinct from all other substances *He only discovers who proves* Otherwise, Paracelsus would be called the discoverer of hydrogen, Lucretius of carbon dioxide, J Kunkel of ammonia, etc D Rutherford (1772) is generally credited with the discovery of nitrogen Rutherford removed oxygen from the air by such combustibles as phosphorus, charcoal, etc, and washed out the products of combustion by alkalies or lime water The residue was called by him "phlogisticated air,"[1] H Cavendish confirmed this experiment in 1785 Lavoisier first called the residue "mephitic air," and afterwards "azote" J A Chaptal (1823) suggested the name "nitrogen" from the Greek νίτρον (nitron), saltpetre, and γεννάω (gennao), I produce—because the gas is a constituent of nitre

Occurrence —Nitrogen constitutes four-fifths of the total volume of atmospheric air According to spectroscopic observations it is probable that certain nebulæ contain nitrogen It is also found in certain minerals, where it is probably occluded or adsorbed It occurs combined in ammonia, nitre, and a great many animal and vegetable products—*e g* white of egg, proteids, etc It is a constant and essential constituent of all living organisms, all life seems to depend upon the *transformation* of proteid compounds

Preparation —Nitrogen is easily obtained from air by removing the admixed carbon dioxide and oxygen This is conveniently done by burning a piece of phosphorus in a dry crucible floating on the surface of water under a small bell-jar The phosphorus combines with most of the oxygen, forming phosphorus pentoxide, and this quickly dissolves in water, leaving behind the nitrogen If the water be alkaline with sodium hydroxide, the carbon dioxide, normally present in air, will also be removed.

[1] Hydrogen was also called "phlogisticated air"

The nitrogen so prepared is not pure because the phosphorus ceases to burn before all the oxygen has been removed. A solution of cuprous chloride (p 249) in hydrochloric acid rapidly absorbs oxygen from air, and leaves behind the nitrogen It is best to remove the carbon dioxide by first passing the air through a solution of sodium hydroxide, and to absorb the oxygen by means of an element which will form a non volatile oxide Copper turnings are generally considered best for the purpose, the "turnings" offer a large surface of oxidizable metal to the air The process is as follows —

Air freed from carbon dioxide in a wash bottle of sodium hydroxide, *A*, Fig 205, and from moisture by passage through sulphuric acid, *B*, is then passsed through a red hot tube containing copper turnings The copper removes the oxygen and forms cupric oxide $2Cu + O_2 = 2CuO$ The nitrogen passes on to be collected in a gas jar, or gasholder, etc In the diagram, the air is supposed to be drawn over the copper, the gas holder being filled with nitrogen If the gasholder were placed at the end *A*, and air forced along the tubes, the nitrogen gas could be collected in

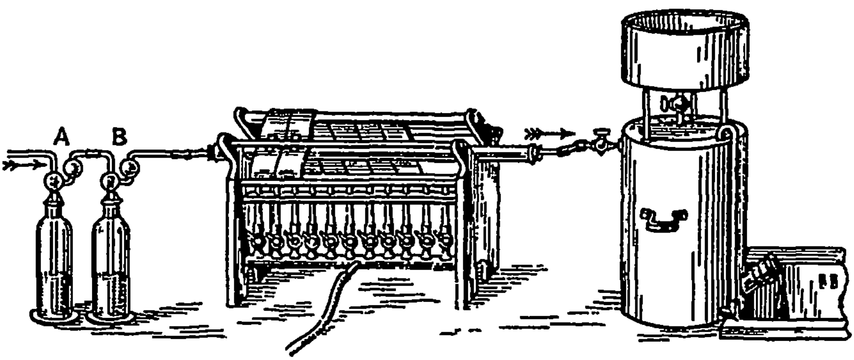


FIG 205 —Preparation of Nitrogen.

gas jars, Fig 205 The process of oxidation of course ceases when all the copper is oxidized If the wash bottle, *B*, of concentrated sulphuric acid be replaced by an aqueous solution of ammonia, as recommended by S Lupton (1876), the ammonia reduces the copper oxide as fast as it is formed · $CuO + 2NH_3 = Cu + 3H_2O + N_2$ Any excess of ammonia can be removed by passing the gas from the copper tube through a solution of sulphuric acid before it is collected in the gasholder Cold boiled water should be used in the gasholder so as to lessen the risk of contamination owing to the presence of oxygen dissolved in ordinary water

We shall see later that "atmospheric nitrogen" contains argon Nitrogen called "chemical nitrogen" can be prepared free from argon by heating a concentrated solution of ammonium nitrite in a glass flask or retort $NH_4NO_2 = 2H_2O + N_2$, or better, a mixture of ammonium chloride with a concentrated solution of potassium or sodium nitrite as recommended by Corenwinder (1849)[1] Atmospheric nitrogen is made

[1] Nitrogen is also made by heating ammonium dichromate $(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2$, or a mixture of ammonium chloride and potassium dichromate, or a mixture of hypobromites or hypochlorites with urea, etc

on a large scale by the fractional rectification of liquid air as indicated on p 126, and it is used in the manufacture of calcium cyanamide, *q v*

§ 2 The Properties of Nitrogen.

Nitrogen is an odourless colourless gas, not quite so heavy as air It is slightly soluble in water, 100 volumes of water at 0° absorb 2 4 volumes, and at 20°, 1 6 volumes of gas Nitrogen has been condensed to a colourless liquid which boils at about −195° at ordinary atmospheric pressure, and solidifies to a white snow-like mass melting at −214° Nitrogen cannot be a poisonous gas, for the air we breathe contains a large proportion The nitrogen dilutes the oxygen as indicated on p 756 Animals die in nitrogen owing to suffocation, *i e.* want of oxygen necessary for respiration Nitrogen is both incombustible and a non-supporter of ordinary combustion

Molecular nitrogen chemically inert, atomic nitrogen active.—The chief characteristic of nitrogen is its chemical inertness, due, it is some times stated, to "the great affinity of the atoms in the molecule for one another" At any rate, when nitrogen is combined with other elements the converse is true, for the nitrogen compounds generally possess great chemical activity Witness nitrogen chloride, possibly the most violent explosive known, potassium nitrate in gunpowder, the white and smokeless powders, and explosives generally—most of them contain nitrogen—NO_2, or NO_3, *e g* nitroglycerol, picric acid, etc

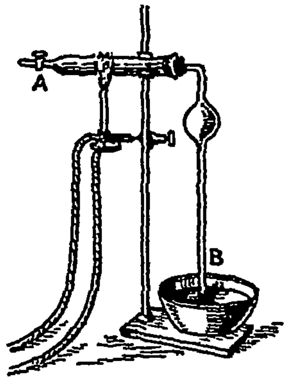


FIG 206 —Formation of Nitrides

Nitrides —Nitrogen combines directly with a few elements under special conditions, *e.g* with calcium, magnesium, lithium, titanium, etc, when these metals are heated in an atmosphere of nitrogen Aluminium, for instance, absorbs 12 2 per cent at 900° The compounds of the metals with nitrogen are called nitrides, just as the corresponding compounds with oxygen are called "oxides" The formation of magnesium nitride can be illustrated by passing nitrogen through the apparatus illustrated in Fig 206 in the direction *AB* A quartz or hard glass tube contains a boat with a little powdered magnesium This tube is connected with a glass bulbed tube dipping in coloured water to serve as gauge When all the air has been expelled by the nitrogen, close the stopcock *A*, heat the tube with a Bunsen's burner, and finally with a large Meker burner, or a blast gas burner When the temperature reaches 900° the bubbling of gas from the tube by thermal expansion will cease, and the rise of the coloured water in the gauge *B* indicates that the metal is absorbing the gas The nitrides of many elements are formed by heating them in ammonia gas

Allotropic nitrogen —About 1820, there was much discussion as to whether nitrogen is an element or a compound Berzelius, for instance, considered nitrogen to be a suboxide of an unknown element which he called "nitricum," but that view was not consistent with the definition of an element So also allotropic modifications of nitrogen have been

reported from time to time, but the allegations have not been established In 1910, R J Strutt noticed that "vacuum tubes" containing nitrogen, when subjected to the jar discharge with a spark gap, show an "after-glow" when the discharge is stopped

The tube AB, Fig 207, is supposed to contain nitrogen. A jar discharge is passed in the direction indicated by the dotted lines shown between the terminals, Fig 207, while the nitrogen travels on towards B The nitrogen is "activated" by the discharge

The nitrogen then appears to be in a more active condition chemically than ordinary nitrogen The activity is not due to the presence of ions produced by the discharge, because the chemical activity of the nitrogen persists after the ions are removed. The "after-glow" which accompanies the conversion of the chemically active modification into ordinary nitrogen is intensified by cooling and weakened by heating The presence of oxygen destroys the activity, hydrogen has no action The active nitrogen gradually returns to normal nitrogen on standing The active modification combines with phosphorus at the same time the excess of phosphorus is converted into the red variety,[1] the "active" nitrogen also combines with sodium, mercury, and acetylene, and with nitric oxide it forms nitrogen peroxide $2NO + N = NO_2 + N_2$ A greenish-yellow flame is developed during the last-named reaction, the flame resembles that produced when ozone reacts with nitric oxide Strutt, the discoverer of these phenomena, suggested as a trial hypothesis, that the "active modification of nitrogen" is nitrogen in the atomic condition, but it cannot yet be said that the action is clearly understood.

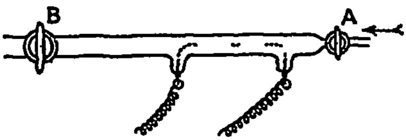


FIG 207—Formation of Strutt's Allotropic Nitrogen.

Atomic weight of nitrogen—The "combining weight" can be determined by finding the amount of hydrogen or oxygen which combines with a known weight of the gas For example, the analysis of nitrous oxide, nitric oxide, ammonia, etc, furnishes O N = 16 14 01 Collect together the vapour densities of all the known volatile compounds of nitrogen We obtain a table from which Table XXXIV has been abridged

TABLE XXXIV—VAPOUR DENSITIES OF VOLATILE NITROGEN COMPOUNDS.

Volatile compound	Vapour density	Formula of compound Molecular weight = vapour density	Amount of nitrogen in the molecule
Ammonia	17 03	NH_3	14 01
Hydrazoic acid	43 04	N_3H	42 03
Nitric oxide	30 01	NO	14 01
Nitric peroxide	46 01	NO_2	14 01
Nitrogen	28 02	N_2	28 02
Nitrous oxide	44 02	N_2O	28 02

[1] It is not uncommon to find some phosphorus converted into red phosphorus when a mass of phosphorus reacts with another substance

The smallest amount of nitrogen entering into the composition of any of these molecules lies somewhere between 14 00 and 14 15, the best representative value is taken to be 14 01, when the atomic weight of hydrogen is 1 008, and of oxygen 16 Hence this number represents the atomic weight of nitrogen

§ 3 The Composition of the Atmosphere

> The air is a confused aggregate of effluviums from such differing bodies, that, though they all agree in constituting by their minuteness and various motions one great mass of matter, yet perhaps there is scarcely a more heterogeneous body in the world —ROBERT BOYLE

These words, written about the middle of the seventeenth century, forcibly impress the fact that air is a mixture of several different gases—oxygen and nitrogen along with much smaller quantities of ammonia and other nitrogen compounds hydrogen, hydrocarbons, hydrogen peroxide, carbon dioxide, sulphur compounds, organic matter, suspended solids, chlorides, ozone, water vapour, argon, helium, krypton, neon, xenon. The last five are sometimes called the "noble gases" or the "inert gases" of the atmosphere, and they are generally included with the "atmospheric nitrogen"

Oxygen and nitrogen —The following analyses are quoted to illustrate the percentage amount of oxygen in air —

Locality	Minimum	Maximum	Mean	Number of analyses	Analyst
Paris	20 913	20 999	20 96	100	V Regnault
Dresden	*20 88*	*20 97*	*20 93*	*46*	W Hempel
Cleveland, Ohio	20 90	20 95	20 93	45	E W Morley

Hence, after making due allowance for differences in the methods of analysis by different men, it is clear that the relative proportions of nitrogen and oxygen in the air collected near sea-level are almost, but not quite, constant. Air at higher altitudes has probably quite a different composition, and A. Weneger (1912) estimates that—

Altitude kilometers	Atmospheric pressure	Hydrogen	Helium	Nitrogen	Oxygen	Argon
0	760	0 0033	0 0005	78 1	20 9	0 937
100	0 0128	67	4	1 0	0	—
500	0 0016	7	—	—	—	—

and he assumes that in the outermost layers a new gas geo-coronium predominates, as is evidenced by the spectra of aurora and of the corona of the sun during an eclipse

Carbon dioxide.—Similar remarks apply to the amount of carbon dioxide This is rather higher in towns than in the open country, but diffusion of air by winds, etc, prevents an excessive accumulation in any part—excluding, of course, badly ventilated rooms Thus, J Reiset (1882) found 3 027 volumes of carbon dioxide per 10,000 volumes of air in Paris, and near Dieppe, 2 942 volumes These numbers may be regarded as normal In towns, during a fog, seven or eight volumes may accumulate, and in badly ventilated rooms, ten times the normal amount of carbon dioxide may be present The other constituents—excluding moisture—are usually regarded as impurities The essential constituents of normal or average air occur in the following proportions —

TABLE XXXV—AVERAGE COMPOSITION OF ATMOSPHERIC AIR

Per cent of	By weight	By volume
Nitrogen	75 51	78 03
Oxygen	23 15	20 99
Inert gases	1 30	0 95
Carbon dioxide	0 04	0 03

Ozone, hydrogen peroxide, and nitrogen oxides—The ozone and hydrogen peroxide are probably formed by electrical discharges in the atmosphere as indicated previously The same remark applies to the oxides of nitrogen Free nitric acid has been reported in the atmosphere of tropical regions, but generally, the nitric acid is combined with ammonia According to A Levy (1889), about 3 lbs of ammoniacal nitrogen, and 1 lb of nitric acid is returned to the earth per acre per annum with the rain In rural districts the soil is said to receive between 4 and 6 lbs of combined nitrogen per acre per annum from the rain

Ammonia—The ammonia in the atmosphere is largely a product of organic decomposition, and *it is returned to the earth by rain in the* form of ammonium nitrate, and sometimes as ammonium sulphate or chloride

Hydrogen and hydrocarbons—A Gautier (1901) found that the air of Paris contains per 100 litres—19 4 c c of free hydrogen, 12 1 c c of methane, 1 7 c c of benzene and related hydrocarbons, and 0 2 carbon monoxide with other hydrocarbons. Gautier's estimate is probably rather high H Henriet (1904) found 2 to 6 grams of formaldehyde per 100 cubic metres of air The presence of hydrocarbons explains the oleaginous character of the deposits which form on roofs, leaves of trees, etc , in towns

Sulphur compounds—A. Ladureau (1883) reported 1 8 c c of sulphur *dioxide per cubic metre in the air of Lille* Sulphur compounds are present in small quantities as hydrogen sulphide, sulphur dioxide, and sulphuric acid in the air of towns. According to R Warrington (1887), about $17\frac{1}{4}$ lbs of sulphur trioxide is annually "poured" upon each acre of land at Rothamsted. G H Bailey (1892) reported a maximum of 0 0267 gram of sulphur estimated as sulphur trioxide in the air near the surface of the ground in Manchester

Chlorine compounds—Rain near the sea brings down a certain amount of chlorine derived from the sea water The proportion of salt in the air is greatest near the sea, and diminishes rapidly further away from the coast E Kinch (1900) found, as an average of twenty six years' observations at Cirencester, that 36 1 lbs. of sodium chloride per acre were brought to the earth with the rain The amount of "wind-borne" sea salt is greatest when the wind blows from the sea Free hydrochloric acid derived from manufacturing operations is sometimes found in the air of towns.

Moisture.—The average amount of moisture, aqueous vapour, in air is rather less than one per cent by volume, it may reach 4 per cent in humid climes The actual amount of aqueous vapour air can carry before it is saturated depends upon the temperature. The higher the temperature, the greater the amount of moisture air can carry (p 157) Air seldom

if ever contains less than one-tenth the possible amount The methods for the determination of moisture in air—hygrometry—are discussed in text-books on physics

§ 4 Is Air a Mixture or a Compound of Oxygen and Nitrogen ?

Let us assume the function of a judge in a law court, and sum up the evidence for the jury

1 The proportions of the constituents of air vary a little in different localities, but even this small variation is not found with pure chemical compounds—law of constant proportions, pp 14, 17 Hence not all the nitrogen and oxygen are combined

2 The atomic proportion of nitrogen and oxygen in air is as 3 77 1, this is approximately as 15 4. Hence if all the nitrogen and oxygen are combined, the formula of the compound is $N_{15}O_4$, or $NO_{0\ 26}$, which does not fit very well with the facts summarized by the law of multiple proportions, p 26 A similar result is obtained by considering the volume relations of nitrogen and oxygen in air—Gay-Lussac's law, p 55

3 The characteristic properties (refractive index, absorption of radiant heat, etc) of nitrogen and oxygen are modified in air only so far as obtains when nitrogen and oxygen are *mixed* in the same proportions The properties of the two gases are not changed so much as would be expected if a chemical compound were formed

4 No heat, no change of volume, or any other sign of chemical change is observed when air is made artificially by mixing the gases together in the right proportions "If a measurable physical property were different in air and in an equivalent mixture of the constituents of air, the conclusion would follow that air is a compound" (H. St C Deville)

5 The constituents of air can be separated by mechanical means *e g* solution in water (p 676), by atmolysis (p 107), and by allowing liquid air to vaporize, when the nitrogen distils off before the oxygen (p 126)

Not one of these five reasons is in itself conclusive, but all, taken together, form a chain of circumstantial evidence which would lead an unbiassed jury to return the verdict Air is a mechanical mixture of nitrogen, oxygen, etc.

§ 5 The Analysis of Air.

Gravimetric process—The gravimetric analysis of air was made by J B A. Dumas and J Boussingault (1841) in an apparatus similar in principle to that illustrated in Fig 208 where a modern furnace is shown in place of the old charcoal furnace, and the number of drying tubes has been reduced A large globe was evacuated, closed, and weighed in that condition This globe was connected as indicated in Fig 208, with a tube containing metallic copper also evacuated, closed, and weighed The copper tube was connected with a series of bulbs, and tubes containing concentrated sulphuric acid to remove moisture and ammonia from the air, and with potassium hydroxide to remove carbon dioxide—only a few of the tubes used by Dumas and Boussingault are shown in the diagram. The tube containing the copper was heated red hot, and air allowed to enter slowly by gradually opening the stopcocks The air on its way to the glass globe was deprived of all but the nitrogen (atmospheric)

When the globe was full, the apparatus was cooled, and the globe and copper tube weighed The increase in weight gave the amount of nitrogen in the globe The tube was also weighed Its increase in weight represented the weight of oxygen which was associated, as air, with the nitrogen in the glass globe, the tube also contained some nitrogen The tube was therefore exhausted and weighed again The difference between the second and third weighings of the tube was taken to represent the nitrogen which must be added to the nitrogen in the globe The amount of oxygen

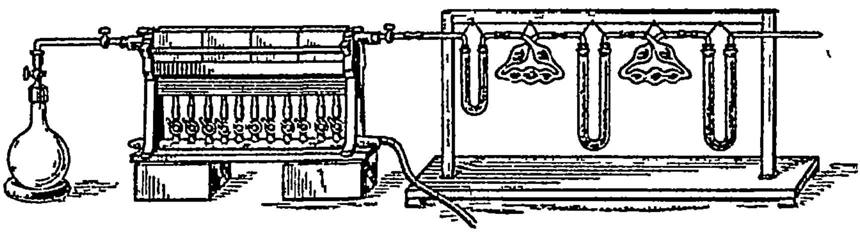


Fig 208 —Diagram illustrating the Principle of Dumas and Boussingault's Method for the Gravimetric Analysis of Air

was calculated from the difference between the first and last weighings of the tube, thus

	Grams
Tube after experiment	651 415
Evacuated tube before experiment	647 666
Evacuated tube after experiment	651 346
Nitrogen	0 069
Total oxygen in tube	3 680
Globe with nitrogen at 19°, 762 7 mm	1403 838
Evacuated globe at 19 4°, 762 7 mm	1391 534
Nitrogen in balloon	12 304
Nitrogen in tube	0 069
Total nitrogen	12 373

Hence in air, the oxygen is to the nitrogen as 3 682 : 12 373, that is as 22 92 : 97 08 As a mean of six determinations they obtained 23 005 grams of oxygen per 76 995 grams of nitrogen The gravimetric process is very exact The error need not exceed 0 00001th part of the whole, but the experiment requires special apparatus, and occupies much time Volumetric processes are not so exact, but they occupy far less time

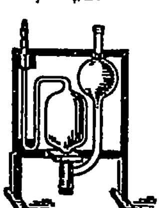


Fig 209 —Absorption Pipette

Volumetric processes —The methods employed by Lavoisier, indicated on pp 9 and 10, are only rough approximations Hempel's method, with an absorption pipette, charged with sticks of phosphorus, Fig 209, gives better results After the air has been measured in Hempel's burette, Fig 32, it is transferred to the pipette where the oxygen is absorbed, and then transferred back to the burette for re measurement The explosion process indicated on p 521, for nitrous oxide, may also be employed

An apparatus, Fig 210, similar to that designed by P von Jolly (1879)

can be used A glass globe is provided with an arrangement whereby a piece of copper wire can be heated red hot while inside The globe is fitted with a three way stopcock which connects it with the gas-measuring tubes or with the outside air The gas-measuring tubes are filled with mercury, and the globe is then connected with the air-pump, and exhausted A jacket containing iced water is placed around the globe Air dried by passage through wash-bottles containing sulphuric acid is allowed to enter the globe, which is then put in communication with the gas-measuring tube, and the level of the mercury in the levelling tube is read when the mercury in the other tube reaches the mark just below the stopcock. Call this position p_0 The cold jacket is then removed, and the copper wire heated. When the oxygen is all converted into copper oxide, again place the cold jacket in position, and alter the levelling tube until the mercury reaches its former position The height of the mercury in the levelling tube is again read Call this position p The pressure of the mercury has been reduced $p_0 - p$ owing to the removal of oxygen Consequently, since the temperature is the same in both cases, the percentage x of oxygen in the air must be $p_0 : p_0 - p = 100 : x$

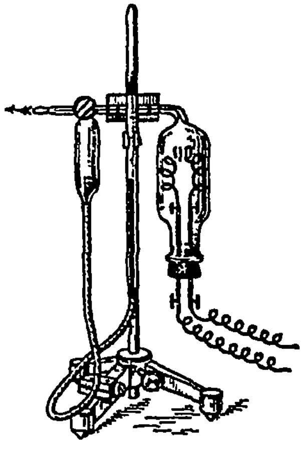


FIG 210 — Jolly's Apparatus for the Volumetric Analysis of Air

§ 6 Argon and its Companions

Atomic weight, A = 39 9; molecular weight, A = 39 9 Melting point, −187 9°, boiling point, −186 1°, critical temperature, −117 4° Vapour density (O_2 = 32) 39 914, (air = 1) 1 3785 A litre of argon under normal conditions weighs 1 78376 grams

The discovery of argon —During 1893–95 Rayleigh found that the density of nitrogen derived from the atmosphere by removing the impurities, ammonia, carbon dioxide, moisture, and also the oxygen, was 14 070 (hydrogen unity), and when the nitrogen was prepared from nitrous oxide, nitric oxide, ammonium nitrite, urea, or magnesium nitride, the density was 14 005 The difference is much larger than the experimental error involved in the determination, and it was therefore inferred that the nitrogen of the air must contain another gas—allotropic nitrogen, or some new gas—previously overlooked The disturbing gas was isolated by W Ramsay in May, 1894 It proved to be a new gas which was named argon—from the Greek ἀργός (argos), inert, idle

Isolation of "argon"—The new gas can be obtained by passing atmospheric nitrogen over heated magnesium, or over a mixture containing one part by weight of magnesium filings, 0 25 sodium, and five of quicklime The magnesium reacts with the quicklime liberating calcium, which absorbs the nitrogen and also any oxygen which may be present Argon can also be prepared by passing air through a hot tube containing calcium carbide at about 800° The oxygen is absorbed $2CaC_2 + O_2 = 2CaO + 4C$, and the nitrogen forms cyanamide $CaC_2 + N_2 = CaCN_2 + C$. The

carbide is said to be much more active if it be mixed with 11 per cent of calcium chloride

Rayleigh also passed a series of electric sparks through a mixture of air and oxygen (p 508), and removed the nitrogen oxides as fast as they were formed by alkalies About $\frac{1}{84}$ of the atmospheric nitrogen remains as a residue which will not combine with the oxygen when sparked in the presence of alkalies This process for isolating the inert gas from air is particularly interesting because H Cavendish made a similar experiment in 1785, and concluded that if any part of the nitrogen of atmospheric air differs from the rest "we may safely conclude that it is not more than $\frac{1}{120}$ of the whole" Remembering the conditions under which Cavendish's experiment was made, this estimate is remarkably close to Ramsay's number, $\frac{1}{84}$ Cavendish's observation was overlooked until Rayleigh and Ramsay indicated its importance

Properties of argon —Argon gas is without colour, taste, or smell It is incombustible and a non supporter of combustion Argon is remarkable in forming no well defined compounds with other elements. 100 volumes of water at 0° dissolve 4 47 volumes, and at 20°, 2 86 volumes Hence argon is rather more soluble than air in water, and in consequence, when the gases dissolved in rain water are expelled by boiling, the resulting "air" is slightly richer in argon than ordinary air Argon is present in the gases from sea water, rivers, and springs, as well as occluded in certain minerals clèveite and uraniferous minerals. It also occurs in rock salt and in some meteorites

The inert gases —Argon isolated from atmospheric air as described above is contaminated with minute quantities of some other gases, for if the liquefied gas be fractionally distilled, Ramsay found that four other gases could be obtained helium—named from Greek ἥλιος (helios), sun, neon—from νεος (neos), new, krypton—from κρυπτός (kryptos), hidden, and xenon—from ξένος (xenos), stranger The neon, helium, argon, and contaminating nitrogen pass off first, the xenon and krypton remain The more volatile gases are compressed in a vessel cooled by liquid air By repeated fractionation of the less volatile residual liquid, the xenon and krypton can be separated from the argon and from one another Similarly, neon and helium can be separated from the contaminating nitrogen and argon By surrounding the mixture of helium and neon with liquid hydrogen, the neon freezes to a white solid from which the helium can be removed by the air pump The physical properties of these gases are summarized in Table XXXVI (p 565)

Like argon, they are all inert chemically, no well defined compounds with other elements have been obtained Hence it is generally stated that these elements are null-valent. These gases can be excited electrically so as to furnish characteristic and complex spectra Ordinary molecular nitrogen, as we have seen, is somewhat inert to ordinary chemical influences, while in the atomic condition it is one of the most active of elements. Accordingly, H E Armstrong (1895–1912) argued that it is possible that the molecules of the inert gases are made up of two or more atoms so firmly bound together that they cannot be severed by any known chemical process The evidence for the familiar statement "The molecules of the inert gases are monatomic," as we shall soon see, is not conclusive Neon has been shown, by atmolysis, to be a mixture of two other gases of atomic weight 19 9 and 22 1 respectively, but no difference has been detected in the physical properties of the two fractions

TABLE XXXVI —PHYSICAL PROPERTIES OF THE INERT GASES

Gas	1000 vols air contain approximately	Density $O_2 = 32$ atomic [and molecular] weight	Melting point	Boiling point	Critical temperature
Helium, He	0 0014	3 99	—	−268 7°	−268°
Neon, Ne	0 015	20 2	−253°	−233°	−220°
Argon, A	9 37	39 88	−188°	−186°	−117°
Krypton, Kr	0 00005	82 92	−169°	−152°	− 63°
Xenon, X	0 000006	130 22	−140°	−109°	+ 15°

Helium —In 1868, P J C Janssen detected a prominent orange line in the spectrum of the sun's photosphere This did not correspond with the spectral lines of any known element Hence E Frankland and J N Lockyer postulated the existence of a new element which they called helium. The same orange line was later detected in the spectrum of certain stars, and in 1882 Palmer noticed the same line in the spectrum of the gases flaming from Vesuvius While seeking for occluded argon in the "nitrogen" which had been reported in many minerals — clèveite, fergussonite, bröggerite, uraninite, etc —W Ramsay found that the gas was neither argon nor nitrogen The spectrum of the new gas was identical with that reported by Janssen and by Palmer Hence its name, helium The same gas was later detected in the gases dissolved in certain mineral waters and also in atmospheric air as indicated above By the rapid evaporation of liquid helium a temperature within 2° of absolute zero −273°, has been obtained by H K Onnes (1908)

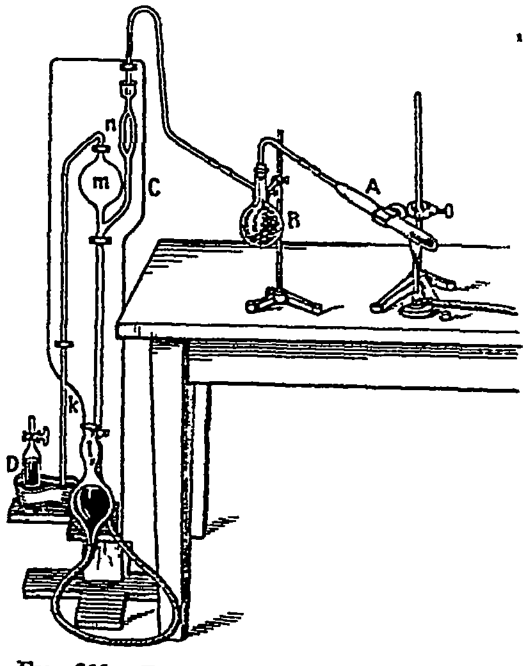


FIG 211 —Removal of Occluded Gases from Minerals

Removal of the gases occluded in minerals —To remove the occluded gases from minerals, the pulverized mineral is heated in a hard glass tube, *A*, Fig 211, with or without concentrated sulphuric acid, or sodium pyrosulphate The system is fitted as shown in Fig 211, and exhausted by

means of an air pump, Toepler's mercury pump,[1] C, is shown in Fig 211 The mineral is heated under reduced pressure, and the gases are collected in D, the receiver of the pump The gases on their way to the pump travel through a flask, B, containing sticks of solid potassium hydroxide to absorb water and sulphur compounds The gas collected in the gas holder D can then be analyzed, or freed from hydrogen and hydrocarbons by passage over hot copper oxide, from oxygen by passage over hot copper, from carbon dioxide by soda lime, or potassium hydroxide, from nitrogen by hot magnesium, ~~and~~ from moisture by phosphorus pentoxide—and the ~~residue~~ examined by the spectroscope for helium, etc The helium occluded in monazite sand can be readily obtained by this process

§ 7 The Two Specific Heats of Gases

It will be remembered that "specific heat" is a term employed to represent the amount of heat required to raise the temperature of one gram of a substance 1° A gas can be heated by simple compression its specific heat must then be zero, but a certain amount of energy, equivalent to the specific heat, is needed for the work of compression Again, a gas, if it be expanded, is cooled, if the cooling effect of expansion just counterbalances the heat added to the gas, the temperature remains constant, and the specific heat appears to be indefinitely large Here work, equivalent to the heat supplied, is performed by the expanding gas These facts show that the condition of the gas must be stated before it is possible to define its specific heat It is conventionally agreed that if the gas be allowed to expand during a change of temperature so that its pressure remains constant, the amount of heat required to raise the temperature of one gram of the gas 1° shall be called the specific heat under constant pressure, and symbolized by C_p If the pressure be increased so that the volume remains constant when the gas is heated, the amount of heat required to raise the temperature 1° is likewise called the specific heat under constant volume, and symbolized C_v

In the following discussion, it will be remembered that the kinetic theory assumes that the temperature is proportional to the average speed of translation of the moving molecules—an increase of the speed is accompanied by a rise of temperature, and conversely The heat imparted to a gas is not spent merely in raising the temperature of the gas, that is, in speeding up the motions of the molecules Energy is spent in—

(1) Augmenting the speed of the moving molecules —The heat required to actually increase the kinetic energy of the moving molecules so as to produce a rise of temperature is the same for all gases. Let a denote this quantity

(2) Performing external work —Heat energy is needed to overcome the pressure of the atmosphere when the gas is allowed to expand Call this quantity b Since the coefficient of thermal expansion of all gases

[1] Toepler's pump C, is worked by raising the levelling tube, l, air is expelled from the exit tube, k, by the mercury rising in m The levelling tube is again depressed, part of the air in AB enters the globe m The air in m is expelled by again raising the levelling tube l, until a little mercury runs down the tube k, the valve n prevents mercury running back into B These operations are repeated until the required degree of exhaustion has been attained

is the same (p 83), this quantity is practically constant for equal volumes or equimolecular weights.

(3) Performing internal work.—Heat energy is required to produce changes within the molecule which may alter the motions or orientation of the constituent atoms of the molecule, or raise the kinetic energy of the atoms moving within the molecule Let c denote the energy spent within the molecule per degree rise of temperature A certain amount of energy must also be spent in overcoming the effects of intermolecular attractions (p 124) This can be neglected for the time being

The ratio of the two specific heats may now be written

$$\frac{C_p}{C_v} = \frac{a + b + c}{a + c}$$

The specific heat of a gas at constant volume—We have seen, p 115, that $pv = \frac{1}{3}MV^2$ where M denotes the mass, and V the average velocity of the molecules But the kinetic energy of a body of mass M moving with a velocity V is $\frac{1}{2}MV^2$, hence $pv = \frac{2}{3} \times \frac{1}{2}MV^2$, or the kinetic energy of the molecular motions is $\frac{3}{2}pv$ But $pv = RT$, p 85 Hence the kinetic energy of molecular motion is $\frac{3}{2}RT$ If one gram of gas be heated 1°, the kinetic energy becomes $\frac{3}{2}R(T + 1)$ Hence if the gas be heated 1° at constant volume, the thermal value of the increased kinetic energy is $\frac{3}{2}R(T + 1) - \frac{3}{2}RT = \frac{3}{2}R$ cals This result represents the specific heat of the gas at constant volume, or, $C_v = \frac{3}{2}R$

The external work done by an expanding gas—Again, if a gram of gas expands against atmospheric pressure when its temperature is raised 1°, the gas, in consequence, does work by pressing back the atmosphere, so to speak The equivalent of this work must be supplied in the form of heat This work is equivalent to the product of the pressure against the change in volume Let x denote the change in volume when the gas is heated 1°, under a constant pressure, then, $p(v + x) = R(T + 1)$, and $pv = RT$, p 85 By subtraction $px = R$ This means that when a gram of gas is heated 1°, the resulting expansion against atmospheric pressure does work equivalent to R cals

The specific heat at constant pressure—Hence, R cals must be added to the previous result to obtain the thermal equivalent of the energy supplied to one gram of gas in the form of heat when its temperature is raised 1° Otherwise expressed, if one gram of gas be heated 1°, at constant pressure, an amount of heat equivalent to $\frac{3}{2}R + R = \frac{5}{2}R$ is required This result represents the specific heat of the gas at constant pressure, or $C_p = \frac{5}{2}R$

The ratio of the two specific heats of a gas—Returning to the ratio of the two specific heats, which is usually symbolized γ, we can now write $a = \frac{3}{2}R$, and $b = R$, or

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R + c}{\frac{3}{2}R + c}$$

The magnitude of c will vary with different gases, for it will naturally be related somehow with the complexity of the molecule The greater the value of c, the less the value of the ratio of the two specific heats. For a monoatomic gas, c is probably zero, and the numerical value of the ratio becomes $\gamma = \frac{5}{3}$, or 1·67 The greater the complexity of the molecule, the

greater the value of c, and the smaller the value of the ratio of the two specific heats This is illustrated by the following table

TABLE XXXVII —RATIO OF THE TWO SPECIFIC HEATS OF GASES.

Gas	Molecule	Atoms per molecule	γ	Gas	Molecule	Atoms per molecule	γ
Mercury	Hg	1	1 67	Carbon dioxide	CO_2	3	1 31
Argon	A	1	1 65	Nitrous oxide	N_2O	3	1 31
Hydrogen	H_2	2	1 41	Hydrogen sulphide	H_2S	3	1 31
Nitrogen	N_2	2	1 41	Ammonia	NH_3	4	1 30
Oxygen	O_2	2	1 40	Methane	CH_4	5	1 27
Carbon monoxide	CO	2	1 40	Ethylene	C_2H_4	6	1 24
Hydrogen chloride	HCl	2	1 [illegible]9	Ethane	C_2H_6	8	1 18
Chlorine	Cl_2	2	1 32	Alcohol	C_2H_5OH	9	1 13
Bromine	Br_2	2	1 29	Benzene	C_6H_6	12	1 0[illegible]
Iodine	I_2	2	1 29	Ether	$C_4H_{10}O$	15	1 06
Iodine chloride	ICl	2	1 31	Turpentine	$C_{10}H_{16}$	26	1 03

The ratio of the two specific heats and molecular weights — These numbers mean that if the ratio of the two specific heats of a gas be about 1 6, the gas will usually have one atom per molecule, with a ratio about 1 4, two atoms per molecule, and about 1 3, three atoms per molecule The kinetic theory would have no explanation to offer if the value of γ were greater than $1\frac{2}{3}$, but no cases are known There are a number of discrepancies This must be expected owing to differences in molecular attraction, tendencies to polymerization, dissociation, etc, which affect the value of c The coloured gases—chlorine, bromine, iodine, and iodine chloride, with two atoms per molecule—give lower values than is usually obtained with the colourless diatomic molecules, and gases which are readily condensed to liquids give rather lower values than those less readily liquefied Hence if the ratio of the two specific heats of a gas falls into one of these groups—1 6, 1 4, 1 3—this fact may be taken as circumstantial evidence, but not conclusive proof, that the molecule has a corresponding number of atoms per molecule The ratio of the two specific heats of argon and the inert gases appears to be about 1 6, and hence it is supposed that the molecules of these gases are monatomic, like mercury This means that the density ($H = 2$), the molecular weight, and the atomic weight will probably have the same numerical value Hence the determination of the ratio of the two specific heats[1] provides an independent method of ascertaining the number of atoms in the molecules of a gas without reference to the compounds of the element In the case of mercury, the monatomicity of the gas has been established altogether apart from this reasoning

This subject cannot be passed by without bringing the weak step in the above reasoning into prominence The low molecular heats of the

[1] The value of γ can be determined experimentally by measuring the velocity of sound in gases For this see any text book on Physics

inert gases are assumed to prove that these gases have one-atom molecules But it is easy to see that if little or no heat is expended in doing internal work when the temperature of these gases is raised, a gas with polyatomic molecules might be reported to have monatomic molecules Unlike mercury, the inert gases do not form chemical compounds, and hence the number of atoms in the molecule cannot be determined by the usual methods based upon Avogadro's hypothesis The inference that the molecules of the inert gases are monatomic thus involves an assumption which is less readily granted than is the case with mercury, cadmium, etc , which do form volatile chemical compounds.

§ 8 The Specific Heats of Elementary Solids—Dulong and Petit's Rule

The atomic heat, that is, the thermal capacity of the atoms of an element, is the product of the specific heat and atomic weight of the element P L Dulong and A. T Petit (1819) in their study of the specific heats of different solid elements obtained a remarkable result They found The product of the atomic weight, w, and the specific heat, c, of an element has nearly always the same numerical value—6 4, or say 6—Dulong and Petit's rule This means that the atomic heats or the thermal capacity of the atoms of the elements are approximately the same The relation is usually expressed

$$\text{Atomic heat} = Cw = 6\ 4.$$

In illustration, a few elements may be selected at random from a list containing nearly 50 elements for which data are available

TABLE XXXVIII —ATOMIC HEAT OF ELEMENTS

Element	Specific heat	Atomic weight	Atomic heat
Lithium	0 9408	6 94	6 53
Silver	0 0559	107 88	6 03
Gold	0 0304	197 2	6 25
Copper	0 0923	63 57	5 88
Bismuth	0 0305	208 0	6 34
Lead	0 0315	207 10	6 52
Aluminium	0 2143	27 1	5 81
Iron	0 1098	55 85	6 12
Uranium	0 0277	238 5	6 61

The atomic weights here range from 6 94 to 238 5, and yet, when multiplied by the respective specific heats, the products are nearly constant Rigorous agreement cannot be expected. The divergencies are too large to be accounted for by the inevitable errors of observation involved in measuring the specific heats, but the very irregularity of the divergencies leads to the view that Dulong and Petit's law approximates to a truth, and that the observed differences are due to disturbing effects which are not functions of the atomic weight—*e.g* crystalline form

Influence of temperature on the atomic heats of carbon, silicon, boron, and beryllium—Silicon, boron, beryllium, and carbon, at ordinary temperatures, have atomic heats represented respectively by 4 8, 2 6, 3 4,

and 1 35, but at higher temperatures these elements approximate close to 6 This is illustrated by the diagram, Fig 212, which represents the influence of temperature on the atomic heats of the elements named The specific heats of silicon, boron, beryllium, and carbon change with temperature, until a point is reached at which they are nearly constant This point is near 600° for carbon and boron, and about 200° for silicon The atomic heats of the elements generally, diverge as the temperature falls, and converge towards a constant value as the temperature rises, e g

	−150°	−100°	−50°	0°	50°
Silver	4 97	5 46	5 80	6 03	6 06
Gold	5 25	5 54	5 78	5 97	6 10
Bismuth	5 49	5 67	5 86	6 06	6 27
Aluminium	3 71	4 54	5 19	5 68	5 89

Some believe that the divergencies are mainly due to the fact that the temperatures at which the specific heats have been determined stand in a different relation to their points of fusion Lead, for instance, at the temperature of boiling water, is much nearer its fusion temperature (327°) than iron (melting at 1530°) would be, but in the case of many elements, the specific heat does not change very much with such small changes of temperature A more likely explanation is to assume that the divergencies are due to differences in the configuration or orientation of the oscillating molecules or the atoms of the solid elements We have seen that the heat required to raise the temperature of a body, according to the kinetic theory, is spent in raising the kinetic energy of the molecules, and probably also in raising the kinetic energy of the constituent atoms, in raising the volume of the body, and in overcoming molecular attractions The coefficient of thermal expansion of solids is small, and therefore also the work of expansion of solids against external pressure is small The difference between the specific heats of a solid and gaseous element is usually great Thus iodine, gas, has an atomic heat 3 3, and iodine, solid, 6 9, bromine, gas, 4 7, bromine, solid, 6 7 Variations in the complexity of the molecules of an element lead to similar differences. Thus the specific heat of amorphous carbon is 0 2609, graphite, 0 2000, and diamond, 0 1470, the specific heat of ordinary tin is 0 0559, and of allotropic tin, 0 0545 Similarly, differences in the physical condition may also produce an effect on the specific heat Thus the specific heat of hard tempered steel is 0 1175, and of soft tempered steel, 0 1165 Consequently, it must be inferred that the heat does important work other than merely raising the kinetic energy of the

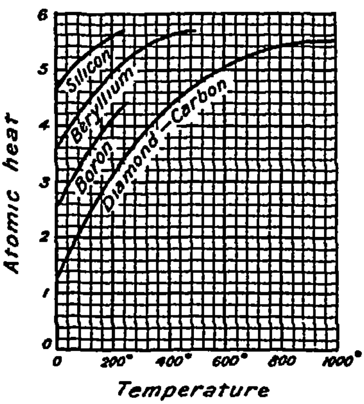


FIG 212 —Effect of Temperature on Atomic Heat Curves

molecules It is therefore strange that the relation pointed out by Dulong and Petit does not exhibit greater divergencies

The rectification of atomic weights by Dulong and Petit's rule. $Cw = 6\ 4$ It will be obvious that if the specific heat of an element be known, it is possible to compute an approximate value for the atomic weight The number so obtained may be useful for deciding between two numbers which are multiples of a common factor The method is obviously only applicable to elements whose specific heat can be determined A E Tilden (1900–3) tried unsuccessfully to find the conditions of temperature for which Dulong and Petit's law holds absolutely Hence he concluded that the usual application of this law to the rectification of atomic weights "is a rough empirical rule, which, setting aside silicon, boron, beryllium, and carbon, is only available when the specific heats have been determined at comparatively low temperatures, usually and most conveniently between 0° and 100°"

EXAMPLES —(1) What is the atomic weight of silver assuming that the specific heat is 0 0559 ? Here, $6\ 4 \div 0\ 0559 = 108$ nearly This is close to the accepted value for the atomic weight of this element

(2) Platinum chloride, on analysis, furnished 35 5 grams of chlorine per 48 6 grams of platinum The specific heat of platinum is 0 0324, and the atomic weight is approximately $6\ 4 - 0\ 0324 = 197\ 5$ Hence, since $197\ 5 - 48\ 6 = 4$ (nearly), it follows that if the atomic weight of chlorine is 35 5, the atomic weight of platinum must be nearly $48\ 6 \times 4 = 194$

(3) When indium was first discovered the analysis of its chloride furnished indium 37 8, chlorine 35 5 The equivalent of indium is therefore 37 8 The formula of the chloride was thought to be $InCl_2$, and the atomic weight was accordingly represented 75 6 The specific heat of the metal was found to be 0 057 Hence, $75\ 6 \times 0\ 057 = 4\ 5$ If 75 6 be the correct atomic weight, the product would approximate closer to 6 4, and hence it was inferred that 75 6 is not the correct atomic weight of indium, rather does the atomic weight approximate to $6\ 4 - 0\ 057 = 112\ 3$ If $InCl_3$ be the formula of the chloride, the atomic weight will be $37\ 8 \times 3 = 113\ 4$, which is the number usually adopted for the atomic weight of this element

§ 9 Molecular Heats

Solids —The molecular heat or thermal capacity of the molecules of a substance is the product of its specific heat and its molecular weight. In 1831 F E Neumann noticed that the product of the specific heat and the molecular weight of compounds of similar composition is nearly constant—*Neumann's law* The value of the constant varies from one series of compounds to another Thus

TABLE XXXIX —MOLECULAR HEATS OF SOLIDS

Carbonates	Mol. wt	Sp heat	Mol heat	Chloride	Mol wt	Sp heat	Mol heat
$CaCO_3$	100 09	0 206	20 6	$BaCl_2$	208 29	0 090	18 7
$SrCO_3$	147 62	0 145	21 3	$SrCl_2$	158 54	0 12	19 0
$BaCO_3$	197 37	0 109	21 4	$PbCl_2$	277 02	0 066	18 3
$PbCO_3$	277 02	0 080	21 3	$HgCl_2$	270 92	0 069	19 2

J P Joule, in 1844, considered that the molecular heat of a solid compound is approximately the sum of the atomic heats of its constituent

elements—Joule's law[1] H Kopp (1865) expressed this by saying that each element has the same atomic heat in compounds as it has in the free state This means that if 6 4 be the atomic heat of each element, and the compound contains n atoms, the molecular heat of the compound will be approximately 6 4n Otherwise expressed, the quotient obtained by dividing the molecular heat of a compound by the number of elementary atoms in one molecule is approximately equal to 6 4 There is obviously a difficulty with the carbonates This is possibly connected with the difficulty previously found for carbon Further, if the atomic heats of all but one of the elements in a compound be known, the unknown atomic heat can be computed, thus, the atomic heat of chlorine in lead chloride is $\frac{1}{2}(18\ 3-6\ 4)=5\ 9$ A comparison of the results of experiment with calculations based upon Neumann's and Joule's laws is indicated in the following table

TABLE XL—MOLECULAR HEATS OF SOLIDS

Compound	Formula	Sp heat	Mol weight	Molecular heat	
				Observed	Calculated
Mercuric chloride	$HgCl_2$	0 0689	270 92	18 67	19 2
Mercuric iodide	HgI_2	0 0420	453 84	19 06	19 2
Mercurous chloride	$HgCl$	0 0520	235 46	12 25	12 8
Mercurous iodide	HgI	0 0385	326 92	12 91	12 9

There are many discrepancies, as might be expected, and for the reasons stated in connection with the atomic heats of the elements

EXAMPLES —(1) Calculate the specific heat of solid oxygen given the specific heat of potassium chlorate, $KClO_3$, 0 194, and that of potassium chloride 0 171 Here the molecular heat of potassium chlorate (molecular weight × specific heat) is 25 7, and of potassium chloride 12 8 The difference $25\ 7-12\ 8=12\ 9$ represents the molecular heat of O_3, hence the atomic heat of oxygen will be $\frac{1}{3}$ of $12\ 9=4\ 3$ By definition, atomic weight × specific heat of solid = atomic heat of solid = 4 3 Hence, the specific heat of solid oxygen will be 4 3 — 16 = 0 27

(2) The specific heat of silver chloride is 0 0911, and that of silver, 0 057 assuming the atomic weight of silver to be 107 9 what is the specific heat of solid chlorine? The molecular heat of silver chloride is 13 1, and the atomic heat of silver is 6 2 The difference $13\ 1-6\ 2=6\ 9$ represents the atomic heat of solid chlorine The specific heat of solid chlorine is therefore $6\ 9 \div 107\ 9=0\ 064$

The molecular heats can be employed to rectify the atomic weights of elements which do not form volatile compounds Thus, the analyses of mercurous and of mercuric salts indicate that the atomic weight of mercury may be 100, 200, If the atomic weight be 100, the formula of mercurous chloride will be Hg_2Cl, and of mercuric chloride, $HgCl$, while if the atomic weight be 200, the formulæ will be those indicated in the above table

[1] This rule is sometimes called after A C Woestyn, 1848; and after H Kopp, 1864–65

EXAMPLES.—(1) The analysis of barium chloride furnishes 35.5 parts of chlorine per 68.7 parts of barium. The specific heat of barium is 0.0465. What is the atomic weight of barium, when the atomic weight of chlorine is 35.5? The formula of barium chloride may be written Ba_xCl, where x is to be determined. The atomic weight of barium, by Dulong and Petit's rule, will be of the order $6.4 \div 0.0465 = 137$. Taking 35.5 as the atomic weight of chlorine, the fraction x must be of the order $68.7 \div 137 = \frac{1}{2}$. Hence the formula of barium chloride is $Ba_{\frac{1}{2}}Cl$, that is, $BaCl_2$, or some multiple of this. Hence the atomic weight of barium (chlorine, 35.5) must be $2 \times 68.7 = 137.4$.

(2) The percentage composition of platinum chloride is: Platinum, 57.7; chlorine, 42.3. The specific heat of platinum is 0.0324. What is the atomic weight of platinum? Hint, see (2) in the last but one set of examples. The ratio of the constituent elements is as 48.6 : 35.5; the atomic weight is of the order 197.5; the ratio x is nearly $\frac{1}{4}$, and hence the formula of the chloride is $PtCl_4$ or some multiple of this. Hence, assuming the atomic weight of chlorine is 35.5, the atomic weight of platinum will be $4 \times 48.6 = 194.4$.

Gases and liquids.—The molecular heats of gases vary according as the specific heats have been determined at constant volume or constant pressure. The ratio of the two molecular heats of gases corresponds with the values determined for the ratio of the two specific heats. The molecular heats of monatomic gases at constant volume approximate to 3; of diatomic gases, to 5; of triatomic gases, $7\frac{1}{2}$, etc. The molecular heats of liquids are generally greater than of the corresponding vapours.

The meaning of Dulong and Petit's rule.—The fact that the atomic heats of all elements are approximately the same, led Dulong and Petit to infer that "the thermal capacity of all atoms is the same." This means that every atom—no matter of what kind, requires the same amount of heat to raise its temperature 1°. Joule's rule means that each elementary atom retains the same capacity for heat when it is combined as it had when free. The number and kind of other atoms present and their mode of combination seem to have no influence on the numerical value of this property. It must be added that we can form no real conception of the "temperature of an atom" or of the "temperature of a molecule." All our conceptions are based on the properties of atoms and of molecules *en masse*. It is often stated that at the "absolute zero" of temperature, −273°, *atomic motion* must cease. This is a mere assertion, of no intrinsic value, and probably wrong. The statement *might* be true of the translatory motion of atom or molecule. According to the kinetic theory, temperature is proportional to the kinetic energy of the molecules; and accordingly, as indicated previously, Dulong and Petit's rule points to a similar relation. The observations of Neumann and Joule indicate that the constituent atoms of a solid compound behave as if the solid were a mechanical mixture of its component atoms, and each atom were free to vibrate independently of the others (see p. 122).

In 1871, L. Boltzmann showed that the kinetic and potential energies of the molecules of a monatomic solid vibrating about a position of equilibrium are equal in magnitude, and that the total energy of the vibrating solid is shared equally between the average kinetic and potential energies, and is twice the value of either alone. If a *monatomic* gas be in contact with a solid with monatomic molecules, the bombardment of the gaseous molecules will produce a state of thermal equilibrium when the mean kinetic energy of the vibrating atoms of the solid is equal to the mean kinetic energy of the translatory motions of the molecules of the gas. It

is shown on p 566 that the kinetic energy due to the molecular motions is $\frac{3}{2}RT$, and therefore the total energy—kinetic and potential—is $2 \times \frac{3}{2}RT$, or $3RT$, where R is nearly equivalent to two calories per gram atom per degree Accordingly, the atomic heat of the solid will be $3R = 6$ nearly Thus Boltzmann arrived at a reasoned explanation of Dulong and Petit's law which had been derived empirically at the beginning of the century Still later, A. Einstein, in 1907, extended to heat an earlier hypothesis of Planck (1906) on the radiation of light The evolution and absorption of energy are not supposed to be continuous processes, but they are assumed to take place *per saltum* in quantities $\epsilon, 2\epsilon, 3\epsilon,$ but not in intermediate amounts $\frac{1}{4}\epsilon, \frac{1}{2}\epsilon,$ The mathematical treatment of this hypothesis gives the expression

$$\text{Atomic heat} = 3R\frac{u^2e^u}{(e^u - 1)^2}$$

where u is written in place of $\beta\nu/T$, and β is written in place of h/k, where k is the atomic gas constant and is equivalent to the ordinary gas constant R divided by the number of atoms per gram atom of gas (approximately $6{\cdot}06 \times 10^{23}$), h is a fundamental constant numerically equal to $6\ 62 \times 10^{-27}$, such that $\epsilon = h\nu$, where ν represents the frequency of atomic vibrations which can be determined from spectrometric observations in the infra red. The magnitude ϵ is called a quantum of energy, and the fundamental hypothesis, the quanta theory of energy When T is large, the correction is small, and the atomic heat reduces to Boltzmann's $3R$ Einstein's formula connecting the atomic heats of solids with their vibration frequencies was very promising, since it gave results in close agreement with observations on the variations of the atomic heats of silver, diamond, etc, over a range of temperature from about $-238°$ to about $900°$ W Nernst and F A Lindemann (1911), P Debye (1913) and others have since improved the fundamental assumptions so much that J H Jeans (1914) could write "The application of the quantum theory to the explanation of low temperature specific heats, from its complete naturalness, and from its agreement with experiment, seems destined to be final"

Questions

1 How may the composition of air be determined? Would the composition of the air be represented either by the formula N_4O or $N_4 + O$? Give reasons for your answer —*Cambridge Senior Locals*

2 State the law of Dulong and Petit and explain its application Discuss its limitations to the determination of atomic weights —*Coll of Preceptors*

3 Classify in some logical way the various components of the air Give proof that the air is a mechanical mixture Explain how nitric acid is manufactured from certain components of the air, and tell why this process promises to be of very great importance —*Princeton Univ U S A*

4 Show (*a*) how a mixture of chlorine and hydrochloric acid may be freed from the latter, (*b*) How hydrochloric acid may be freed from moisture, (*c*) How ammonia may be freed from moisture, (*d*) How a mixture of nitrogen and oxygen may be freed from the latter, (*e*) How a mixture of nitrogen, hydrogen, and hydrochloric acid may be freed from the latter two —*Amherst Coll, U S A*

5 A given volume of air is left in contact with lime (calcium oxide), a second volume of air is shaken up with an acidified solution of ferrous sulphate Carefully describe the changes which occur in the air and in the reagent in each case —*Univ North Wales*

CHAPTER XXX

PHOSPHORUS

§ 1 Phosphorus—Occurrence and Manufacture

Atomic weight, P = 31, molecular weight, P_4 = 124 Ter and quinquevalent Melting point of yellow, 44°, boiling point 290° Specific gravity at 10°, 1 83; vapour density, 127 1 (H_2 = 2), 4 42 (air = 1)

Bone-ash —The animal skeleton is mainly composed of bone Bones contain non-combustible mineral matters, and combustible organic matters Fatty organic matter can be extracted by digesting the bones with solvents like benzene, carbon disulphide, ether, chloroform, etc, which dissolve the fat, and leave behind "degreased bones", the gelatinous matters—glue—can be extracted by digesting the bones with water heated under pressure—"degelatinized bones" remain behind. The degelatinized bones still contain combustible carbonaceous matters, and if they be heated in iron retorts, out of contact with air, gaseous and liquid products distil over, and a residue of "animal charcoal" remains in the retort Dippel's bone oil occurs among the liquid products of the distillation A similar result is obtained if degreased or raw bones be heated in the retorts If animal charcoal, or degreased, degelatinized, or raw bones be heated in air, the organic matters burn, and *bone ash* remains

The manufacture of phosphorus—retort process —If powdered bone-ash be intimately mixed with sulphuric acid, white insoluble calcium sulphate is formed It is best to add just sufficient sulphuric acid to transform all the lime into calcium sulphate The insoluble matters are separated by filtration and washed The clear filtrate is evaporated to a syrupy liquid, mixed with about one-fourth its weight of coke or charcoal, and dried by heating in cast-iron pots The dried mixture is *then heated to redness in fireclay retorts with their necks dipping under the* surface of the water A mixture of hydrogen and carbon monoxide gases escapes, and crude phosphorus condenses as a dark brown solid. From this experiment it is inferred that bone ash is a compound of phosphorus and lime

The chemistry of the process is somewhat as follows Bone ash is a more or less impure form of calcium phosphate, $Ca_3(PO_4)_2$ When this is treated with sulphuric acid, calcium sulphate, $CaSO_4$, separates, and normal phosphoric acid $Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$, or calcium superphosphate, $CaH_4(PO_4)_2$, remains in solution In either case, when the evaporated solution is heated a salt of metaphosphoric acid, HPO_3, is formed $H_3PO_4 = H_2O + HPO_3$, and this, in turn, when heated with carbon, is reduced to the element phosphorus $2HPO_3 + 6C = 6CO + H_2 + 2P$

The manufacture of phosphorus—electrical process—If bone ash be mixed with very finely divided silica and coke, and heated in fireclay retorts to a high temperature, a similar product is obtained. The yield, however, is not so good unless the temperature is inconveniently high. If the mixture be heated in an electrical furnace fitted with carbon rods for conducting the electric current as illustrated in Fig. 213, the production of the high temperature presents no difficulty, and phosphorus distils over. Liquid slag is periodically tapped and run from the bottom of the furnace *D*, and a new charge introduced so that the process is continuous. The charge is fed into the hopper *A*, and thence passes into the chamber *B*, and to the conveyer C, which works something like an Archimedean screw, and carries the charge to the furnace. At the beginning of the operation an alternating current is sent through a pair of thin carbon "electrodes," not shown in the diagram, until the furnace is hot. When heated, the resistance of the furnace is reduced, and a current is sent through the electrodes *E*, and the thin electrodes are withdrawn. The phosphorus vapours and gases escape through a tube *G*. To prevent misunderstanding, it may be necessary to point out that the electric current does its work by raising the temperature of the mass, not by electrolysis.

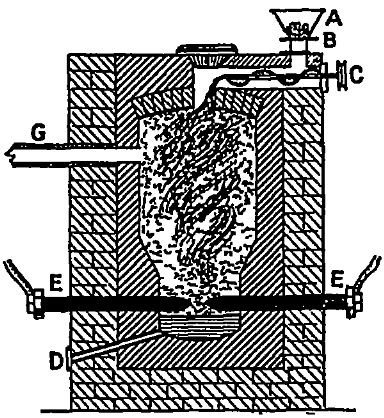


FIG. 213.—Electrical Furnace for the Manufacture of Phosphorus.

The chemistry of the process is somewhat as follows. When calcium phosphate is heated with finely divided silica, SiO_2, calcium silicate, $CaSiO_3$, and phosphoric oxide are produced: $Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5$. The latter is reduced by the carbon: $P_2O_5 + 5C = 5CO + 2P$. The addition of a flux keeps the calcium silicate in a fluid condition and enables it to be tapped from the furnace as a molten slag. The carbon probably accelerates the rate of decomposition of the phosphate by the silica because the reaction progresses more quickly at a lower temperature in the presence of carbon than when carbon is absent. Mineral phosphates (*e.g.* sombrerite) are also used in place of bone ash for the preparation of phosphorus.

The purification of phosphorus.—The crude phosphorus obtained by the processes of manufacture just described, contains carbon and other impurities. The methods of purification used by many manufacturers are guarded as trade secrets. According to the text-books, phosphorus is purified by redistillation from iron retorts, or by warming the phosphorus with a mixture of sulphuric acid and potassium dichromate so as to oxidize some of the impurities; other impurities rise to the surface as a scum, and leave a layer of clear and colourless phosphorus at the bottom of the tank. The molten phosphorus is then allowed to flow into a tube of half-inch bore of such a length that the phosphorus has time to cool before it reaches the end of the tube. The phosphorus is drawn from the tube under water,

and cut into sticks about 7½ inches long Nine sticks weigh about a pound

The occurrence of phosphorus —Phosphorus, of course, does not occur free in nature, because it is so very readily oxidized in contact with air It is, however, rather widely distributed in combination with oxygen —as phosphates—in such minerals as *sombrerite, phosphorite,* and " phosphate rock " (of South Carolina, Florida, and Tennessee), all of which are more or less impure calcium phosphates $Ca_3(PO_4)_2$, in *chlor apatite*—$3Ca_3(PO_4)_2\ CaCl_2$, *fluor-apatite*—$3Ca_3(PO_4)_2\ CaF_2$, *vivianite*—$Fe_3(PO_4)_2\ H_2O$, *wavellite*—$4AlPO_4\ 2Al(OH)_3\ 9H_2O$ It also occurs in *coprolites* The commercial value of these minerals is determined by the amount of phosphorus they contain Some native phosphates are valued for the rare earths associated with the phosphoric acid—*e g* monazite, and some phosphates are present in certain gems—turquoise, lazulite, etc

The phosphorus cycle in nature —Small quantities of phosphates are found in granitic rocks By the weathering and decay of these rocks, the combined phosphorus ultimately finds its way into the soil, spring water, and the sea All fertile soils contain phosphorus, since phosphorus is needed to build up certain essential parts of vegetable tissue The equivalent of one pound of phosphorus is said to be present in about 100 lbs of corn, and in about 1200 lbs of fodder Animals feeding upon plants or upon herbivorous animals concentrate the phosphorus in their bones and tissue The waste of muscular and nervous tissue involves a decomposition of the phosphorus compounds The products of decomposition are carried by the blood to the kidneys, and there excreted with the urine —chiefly as sodium ammonium phosphate Hence phosphorus finds its way back to the soil Hence too the origin of the phosphorus in the large deposits of guano—the excrement of seabirds—on the islands off the Peruvian coast, and a number of islands in the South and the Caribbean Seas. Many islands have been " stripped " from the guano they once contained. Nitrogenous matters and potash, all valuable manures, are also associated with guano The guanos have undergone more or less decomposition by the action of rain, etc , and they are sold on the " per cent. of nitrogen " they contain Some guanos are enriched by the addition of dried blood, ammonium phosphate, etc , and sold as special fertilizers

History —It is generally supposed that phosphorus was accidentally discovered by Brand, an alchemist in Hamburg, between 1668 and 1669, while distilling a mixture of sand and concentrated urine, during his quest for a substance which would turn the base metals into gold We are told that Brand's secret was sold to D Krafft for about £30 It is possible that the secret was communicated to, or else independently discovered by J Kunckel about 1678 A couple of years later, 1680, R Boyle, stimulated by the rumours of the process of preparation by Brand, also found a method of preparing phosphorus similar to that employed by Brand In 1769, G Gahn showed that calcium phosphate occurs in bones, and K. W Scheele, in 1771, obtained phosphorus from bone ash

In the eighteenth century, the term " phosphorus " was applied to substances like commercial barium and calcium sulphides which, after exposure to a bright light, phosphoresce (appear luminous) in the dark. The word " phosphorus " is derived from the Greek—φῶς (phos), light, φέρω (phoro), I carry The term " phosphorus " was naturally applied to

the substance discovered by Brand, because it too glowed in the dark. Terms like "Brand's phosphorus" 'Kunkel's phosphorus' "Boyle's phosphorus," "English phosphorus," "phosphorus mirabilis," and "phosphorus igneous" were used by the early writers on chemistry. Later the term "phosphorus" was restricted to the element phosphorus now under discussion A. L. Lavoisier proved that phosphorus is an element, and he investigated some of the products formed when phosphorus is burned in air

§ 2 The Allotropic Modifications of Phosphorus

It is generally stated that there are two well defined allotropic modifications of phosphorus—yellow and red Many other so called allotropic forms have been described, but there is some uncertainty whether the discoverers have not been deceived by the effect of impurities on the properties of phosphorus Some consider the alleged 'black phosphorus" to be a mixture of phosphorus with some metallic phosphide The allotropy of phosphorus is more complex than is the case with sulphur, and it is not yet possible to give the conditions under which even the better known allotropic forms are stable

The properties of yellow phosphorus —This form of phosphorus has also been called "octahedral,' "common," "colourless,' "white,' and "non-metallic" phosphorus. It is a translucent, almost colourless solid which soon becomes coated with a white opaque crust If exposed to light, yellow phosphorus rapidly darkens in colour At 0° it is hard and brittle with a crystalline fracture, at ordinary temperatures it is soft enough to be cut with a knife It melts at 44° under atmospheric pressure, and at 52 8° under a pressure of 300 atmospheres When molten phosphorus is cooled the temperature can be reduced much below the melting point without solidification, owing to the effects of undercooling Phosphorus boils at 278 3° (762 mm.), and at 165° under a pressure of 120 mm., but it vaporizes at a much lower temperature For instance when phosphorus is heated to 40° in the lower part of a flask in an atmosphere of carbon dioxide, crystals of phosphorus sublime on to the upper part of the flask. Yellow phosphorus also sublimes at ordinary temperatures *in vacuo* when exposed to the light Yellow phosphorus ignites at about 30° in air, saturated with moisture the inflammation temperature is higher the dryer the air When phosphorus burns in air dense white clouds of phosphorus pentoxide, P_2O_5, are formed. If, however, the phosphorus and oxygen be perfectly dried by exposure to the desiccating action of phosphorus pentoxide, phosphorus may be melted and even distilled in oxygen with very little oxidation

The inflammation temperature is so low that the heat of the body suffices to raise the temperature of the phosphorus above its kindling temperature and hence phosphorus should always be 'handled with the forceps, never with the bare fingers unless under water Burns produced by phosphorus are very painful, and heal very slowly The fumes of phosphorus are poisonous. Persons constantly exposed to their action are liable to suffer from caries (rotting) of the bones of the jaw and nose—"fossy jaw' Phosphorus itself is poisonous, it is stated that a 0 1 gram dose is fatal to man.

On account of its inflammability, phosphorus is usually preserved under water in which it is almost insoluble—one part of phosphorus dissolves in 300,000 parts of water, but it readily dissolves in carbon disulphide, sulphur chloride, phosphorus trichloride, etc, and it is also soluble in chloroform, benzene turpentine, alcohol olive oil, etc Octahedral crystals of yellow phosphorus are obtained when the solution in carbon disulphide is allowed to evaporate If a piece of blotting paper be soaked with a solution of phosphorus in carbon disulphide, and the solvent be allowed to evaporate, the finely divided phosphorus which remains behind ignites spontaneously in air owing to its rapid oxidation If a little phosphorus be placed in water, and the water is boiled, phosphorus volatilizes with the steam, if the vapour be passed through a condenser with the apparatus in the dark, a luminous ring appears where the steam condenses If much phosphorus be present, globules of phosphorus will collect in the receiver This is the principle of E Mitscherlich's process for the detection of phosphorus

The oxidization of phosphorus.—When phosphorus is exposed to ordinary air in the dark, it emits a pale greenish light, and gives off white fumes with an unpleasant garlic-like smell The fumes of phosphorus in moist air are mainly P_4O_6, and the glowing or phosphorescence of phosphorus appears to be an effect of oxidation—no oxidation, no glow Phosphorus does not glow at temperatures much below 0°, and not in inert gases—carbon dioxide, nitrogen, etc Phosphorus does not glow in pure oxygen below 15°, but it does phosphoresce if the oxygen be slightly rarefied, or diluted with an inert gas, and the glow in air is stopped if the air be compressed Thus a certain critical pressure of the oxygen is needed to start the phosphorescence The glow in air is stopped if traces of gases which destroy ozone be present—e g hydrogen sulphide, ethylene, turpentine, etc Hence ozone appears somehow to be connected with the phosphorescence Ozone is one product of the oxidation of phosphorus in moist air

The formation of ozone during the oxidation of phosphorus takes place in such a way that the amount of ozone formed is proportional to the amount of phosphorus oxidized, such that the *atomic* ratio Phosphorus oxidized Ozone formed = 1 0 5 It is not clear what actually takes place A great number of more or less plausible hypotheses have been suggested, but a crucial experiment has not been yet devised One hypothesis assumes that atoms of oxygen alone take part in the oxidation, and that some of the molecules of oxygen are dissociated into two atoms, each atom acquires at the same time an electric charge of opposite sign $O_2 = O^+ + O^-$ The phosphorus combines with the atoms with one kind of electric charge, and the atoms of oxygen with a charge of opposite sign form ozone The dissociation of the oxygen molecule is not a consequence of the oxidation, but antecedent to it Another hypothesis assumes that each atom of phosphorus is first oxidized by direct union with a whole molecule of oxygen forming, say, P_2O_2 This then decomposes, giving atomic oxygen $P_2O_2 = P_2O + O$ The atomic oxygen then unites with ordinary oxygen to form ozone According to this view of the reaction, the oxygen molecule is dissociated during the oxidation of phosphorus

The *formation of red phosphorus*.—When yellow phosphorus is exposed to air and light, or when phosphorus is heated to about 250° in an inert gas or *in vacuo*, or when phosphorus is exposed to an electric discharge—silent or spark—it soon passes into a chocolate-red coloured allotropic modification which sometimes has an iron-grey metallic lustre. This variety is called red phosphorus The conversion of yellow into red

phosphorus is conveniently illustrated by sealing up a small piece of yellow phosphorus in a glass tube, *A*, Fig 214, and hanging the tube in the vapour of boiling diphenylamine (boiling point 310°) The vapour of the diphenylamine condenses in the long neck, and runs back into the flask The yellow phosphorus will soon be converted into the red variety The change proceeds with almost explosive violence when the phosphorus is heated under pressure to about 350°, that is about 60° above the boiling point of phosphorus, at 300° the change is moderately fast The speed of the transformation can be accelerated by the addition of a trace of iodine In the presence of this catalytic agent, the change is fairly fast at 200°

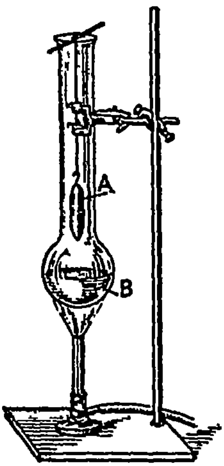


Fig 214 —The Preparation of Red Phosphorus (L Meyer)

The manufacture of red phosphorus—Red phosphorus is made commercially by heating yellow phosphorus in a glass or porcelain vessel embedded in sand placed in a large iron pan The vessel containing the phosphorus is covered with an air-tight lid, and provided with a safety tube dipping in water in case the pressure inside the closed vessel becomes too great When most of the air has been expelled, the safety tube is closed, and the phosphorus is heated until it is converted into the red variety The product of the action is ground with water, and boiled with sodium hydroxide solution so as to remove the unaltered yellow phosphorus The residual red phosphorus is then washed with water, and dried, or preserved wet with water

The transition point red to yellow phosphorus—Red phosphorus is the stable form at ordinary temperatures, and yellow phosphorus the unstable modification The reason the yellow phosphorus does not pass into the red form at ordinary temperatures is due to the extremely slow velocity of the change By the distillation of red phosphorus at 290°, yellow phosphorus is obtained, and at ordinary pressures the transition point of the stable red into the unstable yellow is masked by the vaporization of the phosphorus However, when red phosphorus is heated under pressure in capillary tubes so as to prevent distillation, it forms a yellow fluid at 610°, and red particles begin to separate from the cooling solution at 580° At 570° the mass turns red Red phosphorus melts at 589 5°, under 43 atm pressure The vapour pressure of yellow phosphorus is greater than the red, the curves cannot be carried above 400° because the yellow phosphorus passes into the red variety so quickly at about 400° The two vapour pressure curves are illustrated in Fig 215 Both curves converge towards the melting point as is the case with allotropic modifications of other elements It is inferred that both varieties would be in equilibrium with the vapour phase at the melting point—near 600°—were it not for the disturbing phenomenon just indicated.

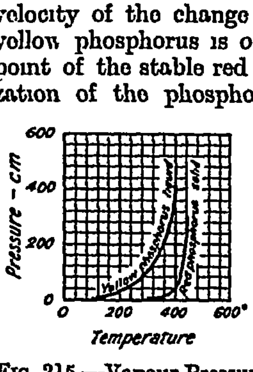


Fig 215 —Vapour Pressure Curves of Phosphorus

Solubility of red phosphorus—Red phosphorus is practically insoluble in the ordinary solvents which dissolve yellow phosphorus Red phosphorus is soluble in phosphorus tribromide, and in alcoholic potash If the solution in phosphorus tribromide be boiled for some time, what is supposed to be a mixture of red phosphorus and phosphorus tribromide separates as a scarlet red powder—Schenk's scarlet phosphorus This resembles red phosphorus in many of its properties, but is rather more chemically active, as might be expected from its extremely fine state of subdivision This variety of red phosphorus has not been prepared free from the solvent in which it is formed When the red-coloured solution of red phosphorus in alcoholic potash is acidified, a red powder is precipitated Some believe that this is nothing but impure red phosphorus, others believe that it is an impure phosphorus suboxide—P_4O The analysis is difficult because of the impurities associated with the precipitate, and hence the question has not been definitely answered.

The crystallization of red and yellow phosphorus—Crystals of yellow phosphorus are obtained by the slow evaporation of a solution of phosphorus in carbon disulphide, or by sublimation *in vacuo* or in an atmosphere of an inert gas Small rhombohedral crystals of red phosphorus are formed by heating ordinary red phosphorus under pressure at 580°, or in a sealed tube with metallic lead at about 500° for about eighteen hours The lead dissolves the phosphorus at the high temperature, and rejects the dissolved phosphorus on cooling in the form of rhombohedral crystals. The lead can be dissolved away by means of dilute nitric acid followed by boiling with concentrated hydrochloric acid. This form of red phosphorus is sometimes called Hittorf's phosphorus, or metallic phosphorus, or "rhombohedral" phosphorus [1]

Chemical properties—Red phosphorus is less chemically active than ordinary yellow phosphorus. This agrees with the fact that the passage of the yellow to the red variety is attended by an evolution of heat $P_{yellow} = P_{red} + 4$ Cals, and hence it is generally stated that red phosphorus contains less available energy than yellow phosphorus Red phosphorus takes fire when heated in air to about 260°, and like yellow phosphorus, previously discussed, it burns, forming phosphorus pentoxide Red phosphorus burns if heated in an atmosphere of chlorine, whereas ordinary phosphorus fires spontaneously in the gas At ordinary temperatures, phosphorus reacts with sulphur, forming phosphorus sulphides, with the halogens, forming tri- or penta-halides, with hot potassium or sodium hydroxide, forming gaseous phosphorus hydrides Concentrated nitric acid is reduced with almost explosive violence, while dilute nitric acid evolves nitrous fumes, boiling sulphuric acid is reduced to sulphur dioxide, etc

Since the amount of heat developed by the combustion of red phosphorus is not constant, it is possible that ordinary red phosphorus is a solution of colourless in rhombohedral phosphorus, or else a mixture of colloidal and "metallic" phosphorus The difference in the molecules of red and yellow phosphorus in not known As is probably the case with monoclinic and rhombic sulphur, it may be due to a difference in the

[1] E Cohen and J Olie (1909) consider red phosphorus to be an isomorphous mixture or a solid solution of yellow and metallic phosphorus in dynamic equilibrium $P_{red} \rightleftharpoons P_{yellow}$ A Smits and H L de Leeuw (1911) consider yellow, red, and metallic phosphorus to be three solids which can form solid solutions with one another

arrangement of identical molecules, or to a difference in the molecular weight, that is, to the number of atoms per molecule Equal weights of red and yellow phosphorus when burnt separately in an excess of oxygen, give equal weights of phosphorus pentoxide, P_2O_5

Phosphides —Phosphorus unites directly with many metals, forming phosphides Metallic phosphides are precipitated by the action of phosphorus on solutions of some metallic salts. Thus silver phosphide, Ag_3P, is precipitated from solutions of silver nitrate, and copper phosphide, Cu_3P_2, from solutions of copper sulphate Tin forms several phosphides when heated with phosphorus. For instance, tin phosphide, Sn_3P, is a coarsely crystalline mass melting at about 170° Tin phosphide is also called "phosphor tin," and it is used in the preparation of manganese bronzes—"phosphor bronze," for example, is made by fusing together copper and phosphor tin The resulting alloy contains from 5 to 15 per cent of tin, and 0 25 to 1 5 per cent of phosphorus This alloy is hard and firm It is remarkably homogeneous, and is specially valuable for the manufacture of axle bearings, etc Calcium phosphide is formed when metallic calcium is heated under naphtha with phosphorus, or by passing the vapours of phosphorus over red hot lime heated in an iron tube The red, brown, or black mass obtained in the last-named reaction is mixed with some calcium pyrophosphate, $Ca_2P_2O_7$

Properties of red and yellow phosphorus —The following table gives a summary of the leading differences in the two varieties of phosphorus

TABLE XLI —COMPARISON OF THE PROPERTIES OF RED AND YELLOW PHOSPHORUS

Property	Red phosphorus	Yellow phosphorus
Colour	Reddish violet	Almost colourless
Crystalline form	*Rhombohedral system*	*Cubic system*
Smell, etc.	Tasteless, odourless	Garlic like smell[1]
Exposed to air	No phosphorescence no oxidation	Phosphorescence and oxidation
Melting point	500° to 600°	44°
Physiological action	Non poisonous	Poisonous
Specific gravity	2 05 to 2 39	1 83 to 1 85
Specific heat	0 170	0 189
Action carbon disulphide	Insoluble	Soluble
Ignition temperature	260°	30°
Electric current	Feeble conductor	Very feeble conductor
Hot sodium hydroxide	Nil	Action
Chlorine gas	Fires if heated	Fires spontaneously
Heat of combustion (Cals)	363 4	370 8

P W Bridgman's study of the effect of high pressures on phosphorus furnished him with an hexagonal variety of yellow phosphorus which passes into the ordinary cubic form at the transition point −76 9°, and a variety of black phosphorus formed at 200° under pressures from 12,000 to 13,000 kilograms per sq cm

Atomic and molecular weight —The atomic weight of phosphorus with reference to oxygen 16, lies somewhere between 30 91 and 31 05 the best representative value is taken to be 31 This has been determined by the analysis of silver phosphate, by the action of phosphorus on silver nitrate, and by the titration of phosphorus trichloride on silver nitrate Vapour density determinations of volatile phosphorus compounds—PH_3, PCl_3, PF_5, etc —show that thirty one is the smallest amount of phos-

[1] When oxidizing

phorus which enters into the composition of any one of these molecules, and hence the atomic weight is 31

The vapour of phosphorus, according to E Mitscherlich, has a specific gravity of 4 58 at 515°, and 4 5 at 1040° Hence the molecular weight of phosphorus is 4 5 × 28 9 = 124 nearly This corresponds with a molecule P_4 Above 700°, the vapour density falls to a number corresponding with a dissociation of the complex molecule $P_4 \rightleftharpoons 2P_2$ The depression of the freezing point of solutions of phosphorus in carbon disulphide also corresponds with four-atom molecule In some other solvents numbers corresponding with P_2, P_4, or with mixtures of P_4 and P_2 are obtained

§ 3 Phosphorus Trihalides

Phosphorus trichloride, PCl_3—This compound is made by passing chlorine, dried by sulphuric acid, over molten white phosphorus in the following manner

A layer of sand is placed at the bottom of a retort, fitted up as illustrated in Fig 157, without the Bunsen's burner and a current of dry carbon dioxide, or another inert gas, is introduced Add, say, 100 grams of yellow phosphorus—dried between filter paper, and dipped successively in alcohol and in ether—then pass a current of chlorine through the apparatus while the retort is heated with warm water The tube delivering the chlorine should be movable, for if it is too near the phosphorus the phosphorus gets hot and distils, forming a red crust in the upper part of the retort, while if it be too far away, the action is slow, and the excess of phosphorus forms phosphorus pentachloride by a side reaction When the action has begun, a tongue of flame projects from the tube delivering the chlorine The retort does not then need heating Towards the end, when the phosphorus has all disappeared, heat the retort very gently so as to drive the trichloride into the receiver The fumes from the exit tube must be led into a stink closet or into a vessel containing sodium hydroxide The product can be purified by adding, say, 2 grams of yellow phosphorus and redistilling The object of the phosphorus is to convert any pentachloride into the trichloride Moisture must be carefully excluded

Phosphorus trichloride is a mobile liquid with an unpleasant smell It boils at 74°, fumes in air, and is hydrolyzed by water forming phosphorous and hydrochloric acids $PCl_3 + 3H_2O = 3HCl + P(OH)_3$ It can be frozen to a solid, melting about −115° The composition of phosphorus trichloride, and also of the other halides of phosphorus, can be determined by treating the compound with water, and determining the amounts of the different acids formed by the regular methods of analysis The lowering of the freezing point of solution of phosphorus trichloride in phosphorus oxychloride, or in benzene, corresponds with the molecular weight PCl_3 Its vapour density, according to J B Dumas, is 140 (O = 32), thus corresponding with the molecule PCl_3 (theoretical vapour density 137 5)

Phosphorus tribromide, PBr_3—Phosphorus tribromide is made by gradually adding a solution of bromine in carbon disulphide to dry red phosphorus The object of the carbon disulphide is to moderate the violence of the reaction The solvent is afterwards distilled off, at about 46°, and the tribromide is distilled, at about 174°—the boiling point of the tribromide The properties of phosphorus tribromide resemble those of the trichloride

Phosphorus triodide, PI_3—This compound is made by dissolving, say, 10 grams of phosphorus in carbon disulphide, and gradually adding the solution to a solution of 123 grams of iodine in carbon disulphide The solvent is then distilled off The triodide remains behind as a

reddish crystalline solid which melts at 41°, and dissociates when heated If 82 grams of iodine be employed per 10 grams of phosphorus, a compound with the empirical formula P_2I_4—called phosphorus di-iodide—remains in the form of orange red crystals, which melt at 110°

Phosphorus trifluoride, PF_3—Phosphorus trifluoride is made by the action of copper phosphide on lead fluoride, or by allowing arsenic fluoride, AsF_3, to drop slowly into PCl_3 with the exclusion of moisture It is a colourless gas which can be condensed to a liquid, boiling at −95°, and frozen to a solid, melting at −160° If a stream of electric sparks be passed through the gas, phosphorus and phosphorus pentafluoride are formed $5PF_3 = 3PF_5 + 2P$, and the pentafluoride, in turn, is said to suffer slight decomposition $PF_5 = PF_3 + F_2$

§ 4 Phosphorus Pentahalides

Phosphorus pentachloride, PCl_5—Phosphorus pentachloride is made by the action of an excess of chlorine upon phosphorus, or by the action of dry chlorine upon the trichloride Since phosphorus pentachloride is a very unpleasant substance to manipulate in air, owing to the fact that it rapidly absorbs moisture, forming hydrochloric and phosphoric acids $PCl_5 + 4H_2O = 5HCl + H_3PO_4$, it is best to make the compound in the bottle in which it is to be preserved Fit the bottle with a three hole stopper, Fig 216—one hole is for the tube bringing in dry chlorine, one for the exit of the chlorine, and the third for a tap funnel by means of which phosphorus trichloride can be run into the chlorine drop by drop

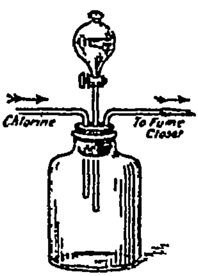


Fig 216 The Preparation of Phosphorus Pentachloride

The vapour pressure of solid phosphorus pentachloride at 140° is 760 mm, and it therefore vaporizes without fusion Phosphorus pentachloride also sublimes below 100° without fusion, but when heated under pressure it melts at about 148° Both phosphorus trichloride and phosphorus pentachloride are valuable reagents for transforming hydroxyl compounds into the corresponding chlorides Each OH group is displaced by an atom of the halogen For example water, H—OH, gives hydrogen chloride, H—Cl, nitric acid, NO_2—OH, gives nitroxyl chloride NO_2—Cl, sulphuric acid, $SO_2(OH)_2$, gives sulphuryl chloride, SO_2Cl_2, alcohol, C_2H_5OH, gives ethyl chloride, C_2H_5Cl, etc

Phosphorus pentabromide, PBr_5—This compound is prepared by a similar process to that used for the pentachloride—the addition of bromine to phosphorus tribromide—and its properties are similar Phosphorus pentiodide—PI_5—has been reported, but there is some doubt as to its real existence

The vapour density of phosphorus pentachloride and pentabromide.—The vapour densities of these two compounds diminish with rise of temperature Thus J B Dumas found for the pentachloride

Temperature	182°	200°	250°	300°
Vapour density	146 6	140 0	115 2	104 8
Amount dissociated	41 7	48 5	80 0	97 3 per cent.

Theory for PCl_5 = 208 5

The vapour density remains practically constant at temperatures exceeding 300° The colour of the vapour becomes yellowish-green at the higher temperatures, showing that free chlorine is probably present; and in the case of the pentabromide, the characteristic colour of free bromine appears. There is little room for doubt that phosphorus pentachloride dissociates into free chlorine (Cl_2, vapour density 71) and phosphorus trichloride (PCl_3, vapour density 137 5) Paper moistened with potassium iodide and starch shows the blue coloration characteristic of free chlorine when the pentachloride is heated to 157° to 158° Assuming that dissociation is complete at 300°, the vapour density should be $\frac{1}{2}(137\ 5 + 71) = 104\ 3$ ($H_2 = 2$), a number very close to the observed value The discussion in connection with the dissociation of nitrogen peroxide shows how the amount of dissociation can be determined from the vapour density at the different temperatures

According to the principles developed in connection with the dissociation of iodine, the dissociation of the pentachloride will be represented by the equation $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ If C_{PCl_5} C_{PCl_3}, and C_{Cl_2} respectively denote the concentrations of phosphorus pentachloride, phosphorus trichloride, and of chlorine, we have, for equilibrium $kC_{PCl_5} = k'C_{PCl_3}C_{Cl_2}$ Suppose that one gram of phosphorus pentachloride be heated in a closed vessel of volume v Let x represent the fraction dissociated at any given temperature, there will obviously be C_{PCl_5}, or $(1-x)/v$ gram-molecules of the pentachloride per unit volume, C_{PCl_3}, or x/v gram molecules of the trichloride, and C_{Cl_2}, or x/v gram-molecules of chlorine Hence for equilibrium, the preceding equation becomes

$$k\frac{(1-x)}{v} = k'\left(\frac{x}{v}\right)^2, \text{ or, } K = \frac{k}{k'} = \frac{x^2}{(1-x)v}$$

Suppose that at 250° 0 80 gram-molecules of the substance are dissociated, then $x = 0\ 8$, and $1 - x = 0\ 2$ Hence $K = 0\ 64 - 0\ 2 = 3\ 2 - v$ One gram-molecule of a gas at 760 mm and 0° occupies 22 3 litres, and at 250° it will occupy 42 7 litres But on dissociation, one gram-molecule of phosphorus pentachloride becomes two gram-molecules of mixed chlorine and phosphorus trichloride Hence if 0 8 gram-molecule of the pentachloride is dissociated, the mixed gas contains $1 + 0\ 8 = 1\ 8$ gram-molecule, so that if one gram-molecule occupies 42 7 litres, 1 8 gram-molecule will occupy $42\ 7 \times 1\ 8 = 76{\cdot}9$ litres Hence $K = 3\ 2 - 76\ 9 = \frac{1}{24}$, or $k\ \ k' = 1\ \ 24$ This means that the phosphorus trichloride and chlorine will unite twenty-four times as fast as the pentachloride will dissociate supposing that each substance has unit concentration, and each action proceeds without reversion, p 268

If the concentration of the phosphorus trichloride or of chlorine be augmented, it is obvious that in order to restore equilibrium, the speed of combination of the chlorine and trichloride must be augmented This is easy to demonstrate (1) from the theory of opposing reactions, (2) from the kinetic theory of dissociation, and (3) experimentally by sealing equal amounts of phosphorus pentabromide in two stout test-tubes, but in one of the tubes also place some phosphorus tribromide When the two tubes are heated under the same conditions, the contents of the tube without the tribromide will have a deeper tint than the tube with the tribromide H. Wurtz, indeed, in 1873, found that if the

pentachloride be volatilized in an atmosphere of the trichloride the vapour density is nearly normal, 206 6, between 160° and 175° The raising of the boiling points of solutions of phosphorus pentachloride in carbon tetra chloride correspond with the formula, PCl_5 The lowering of the freezing points of solutions of the pentachloride in benzene correspond with the molecular weight PCl_5

Phosphorus pentafluoride, PF_5—This compound is made by the action of arsenic trifluoride on phosphorus pentachloride $5AsF_3 + 3PCl_5 = 5AsCl_3 + 3PF_5$ It is a colourless gas which is hydrolyzed by water, forming phosphoric and hydrofluoric acids It can be condensed to a liquid, boiling at —75°, and frozen to a solid, melting at —83° Its vapour density is 126 ($H = 2$), and its formula is therefore PF_5 (vapour density, 126), where phosphorus is undoubtedly quinquevalent

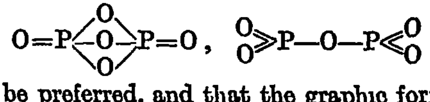
To summarize, the following well defined halides of phosphorus have been prepared

			P_2I_4(solid)
PF_3 (gas)	PCl_3 (liquid)	PBr_3 (liquid)	PI_3 (solid)
PF_5 (gas)	PCl_5 (solid)	PBr_5 (solid)	

Some mixed halide salts—PF_3Cl_2, PF_3Br_2, PCl_3Br_2, etc —have also been isolated

Phosphoryl chloride, phosphorus oxychloride, $POCl_3$—This com pound can be made by very carefully adding water to phosphorus penta-chloride until the solid disappears $PCl_5 + H_2O = POCl_3 + 2HCl$. It is also made by gradually adding, say, 32 grams of powdered potassium chlorate to 100 grams of phosphorus trichloride at ordinary temperatures, and then distilling the mixture The oxychloride boils at 107 2° It can be solidified to a colourless crystalline mass melting at —1 25° It fumes in air, smells like the trichloride, and is slowly hydrolyzed by water, forming phosphoric and hydrochloric acids The corresponding phosphoryl bromide, $POBr_3$, is made in a similar manner, and boils at 190° Phosphoryl fluoride, POF_3, as well as the other phosphoryl compounds can be made by the action of phosphorus pentoxide, P_2O_5, on the halogen acid $4P_2O_5 + 6HF = 2POF_3 + 6HPO_3$

If phosphorus trichloride, PCl_3, be oxidized at a low temperature by treatment with nitrogen peroxide, N_2O_4, among other products, pyrophosphoryl chloride, $P_2O_3Cl_4$, is obtained as a colourless fuming liquid which boils at 210°–215° with partial decomposition into P_2O_5 and $POCl_3$ This mode of preparation is interesting because it shows that two of the oxygen atoms in phosphorus pentoxide probably behave differently from the other three Some take this to mean that of the two formulæ for phosphorus pentoxide



the former is to be preferred, and that the graphic formula for the oxychloride is $O{=}P{\equiv}Cl_3$

Two isomeric oxychlorides of phosphorus can be predicted, in one, $Cl_2{=}P{-}OCl$, the phosphorus is tervalent, and in the other, $O{=}P{\equiv}Cl_3$, quinquevalent, but only one is known On the other hand, two different substances, $PO(C_6H_5)_3$ are known. One (phenoxy-diphenyl phosphine) is a thick oily liquid, boiling at 265° (62 mm), in this the phosphorus is

tervalent and the compound reacts with oxygen, bromine, selenium, and sulphur, and forms additive compounds with alkyl halides The other (triphenyl phosphine oxide) is solid, melting at 153 5°, in this the phosphorus is quinquevalent, and it does not react with the substances just named In both the vapour density corresponds with the empirical formula $PO(C_6H_5)_3$

§ 5 Phosphorus Hydrides, or Hydrogen Phosphides

Phosphine, PH_3 —When phosphorus is heated with caustic alkaline solutions—for instance, milk of lime or a solution of potassium hydroxide —a gas is evolved which ignites spontaneously in air The experiment is made by means of the apparatus illustrated in Fig 217 A mixture of potassium hydroxide solution and yellow phosphorus is placed in the flask fitted with delivery tube, etc, as illustrated in the diagram A current of an inert gas—coal gas, hydrogen, or carbon dioxide—is first led through the apparatus to drive out the air The mixture in the flask is then heated. The phosphorus reacts with the alkali, forming potassium hypophosphite, and gaseous phosphine, PH_3, associated with some impurities The mixture of gases so prepared is sometimes called "phosphuretted hydrogen" The main reaction is represented $3KOH + 4P + 3H_2O = 3KH_2PO_2 + PH_3$ Each bubble of gas rises to the surface of the water, and, when it comes in contact with the air, ignites with a slight explosion and burns with a brilliant flash of light, forming a vortex ring of phosphorus pentoxide, P_2O_5 If the gas be passed through a tube immersed in a freezing mixture, it no longer inflames on contact with the air Indeed, pure phosphine does not inflame spontaneously in air This property appears to be due to the presence of a little of the so called liquid hydrogen phosphide, P_2H_4, as an impurity, when this impurity is removed by condensation in the cold tube, the gas does not ignite when brought in contact with air

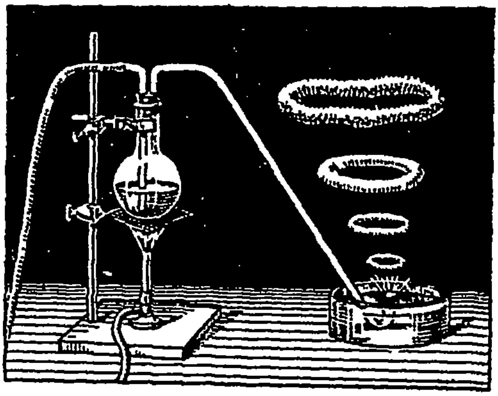


FIG 217 —The Preparation of Phosphine

The properties of phosphine —Phosphine is a colourless gas, smells like decaying fish, liquefies about −85°, solidifies about −133°, and ignites when heated to about 100° It burns in air, forming phosphorus pentoxide $2PH_3 + 4O_2 = P_2O_5 + 3H_2O$ If a mixture of oxygen and phosphine be suddenly rarefied, an explosion occurs The phenomenon recalls the effect of rarefaction on the luminosity of phosphorus in oxygen gas. Nitric acid or chlorine when brought in contact with the gas cause inflammation A jet of phosphine inflames and burns, forming phosphorus pentachloride when placed in chlorine gas $PH_3 + 4Cl_2 = 3HCl + PCl_5$ Phosphine is slightly soluble in water 100 volumes of water dissolve about 11 volumes of the gas The aqueous solution is not alkaline like aqueous ammonia, it decomposes on exposure to light and deposits

red phosphorus The gas possesses reducing properties When passed into solutions of copper sulphate, $CuSO_4$, mercuric chloride, $HgCl_2$, phosphine precipitates phosphides of the metals It combines with ammonia, and some of the chlorides, for instance, aluminium chloride, stannic chloride, etc

The composition of phosphine—J B Dumas determined the composition of phosphine by passing a known volume of the gas over heated copper turnings—zinc, antimony, iron, and potassium have been used in place of copper The copper forms copper phosphide The increase in weight of the copper shows the amount of phosphorus in a given volume of the gas The escaping hydrogen is collected and measured. Experiment shows that 34 parts of phosphine by weight give 31 parts of phosphorus and 3 parts of hydrogen The empirical formula is therefore PH_3 Similarly, when phosphine is decomposed by the passage of electric sparks

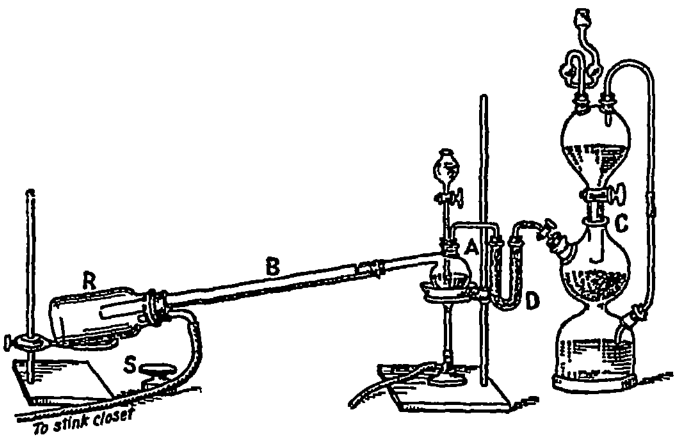


FIG 218—*The Preparation of Phosphonium Iodide*

through the gas (Fig 155), one volume of phosphine gives $1\frac{1}{2}$ volumes of hydrogen, and red phosphorus, of negligibly small volume in comparison with the volume of the gas, is deposited on the walls of the tube Hence two volumes of phosphine furnish three volumes of hydrogen, otherwise expressed, by Avogadro's hypothesis, two molecules of phosphine give three molecules of hydrogen

$$\underset{\text{2 vols}}{2PH_3} = \underset{\text{3 vols}}{3H_2} + \underset{\text{Solid}}{2P}$$

One litre of phosphine weighs 1 52 gram under normal conditions Hence if one litre of oxygen weighs 1 429 gram, the vapour density with reference to oxygen 32 is 33 9, corresponding with the formula PH_3

Phosphonium compounds—When phosphine is brought in contact with hydrogen chloride, hydrogen bromide, or hydrogen iodide, the gases unite, forming a series of so called *phosphonium compounds* $PH_3 + HCl = PH_4Cl$. The chief interest of the phosphonium compounds lies in their relationship to the ammonium compounds which are formed in a similar manner $NH_3 + HCl = NH_4Cl$ The monad radicle, PH_4, phosphonium, bears the same relation to phosphorus that NH_4, ammonium, bears to

nitrogen The basic properties of phosphine are very much feebler than ammonia Phosphonium iodide is one of the best known phosphonium compounds It is prepared in the following manner

Place 100 grams of phosphorus in a retort, *A*, and add an equal weight of carbon disulphide, and then 170 grams of pure iodine Keep the retort well cooled during the mixing Distil off the carbon disulphide by attaching a Liebig's condenser to the retort, and placing the retort in a dish of warm water The retort is then connected with a wide tube, *B*, which may be fitted with a glass bottle, *R*, as shown in Fig 218, and then, in the fume closet, with a wash-bottle containing water to absorb any hydrogen iodide formed by the decomposition of the phosphonium iodide Connect the retort with a Kipp's apparatus, *C*, for generating carbon dioxide, dried by passage through a tube, *D*, charged with pumice stone soaked with sulphuric acid, and keep a slow stream of carbon dioxide passing through the apparatus all the time an experiment is in progress Let 85 grams of water fall slowly, drop by drop, on to the residue in the retort The heat of the reaction suffices to sublime the phosphonium iodide into the wide tube, but towards the end of the operation, the retort may be warmed When the operation is completed, loosen the phosphonium iodide which has collected in the wide tube by means of a piece of wire, and transfer the salt to the bottle used as a receiver The bottle is then closed with its stopper, *S* The reaction is represented $5I + 9P + 16H_2O = 5PH_4I + 4H_3PO_4$

Phosphonium iodide crystallizes in large quadratic prisms with a brilliant lustre It is an unstable salt readily dissociating into hydrogen iodide and phosphine, even at as low a temperature as 30° The crystals can be sublimed without melting They fume in air, and in contact with water form hydrogen phosphide and hydrogen iodide With potassium hydroxide, pure phosphine is obtained $PH_4I + KOH = KI + H_2O + PH_3$, and with alcohol C_2H_5OH, a similar reaction takes place $PH_4I + C_2H_5OH = C_2H_5I + H_2O + PH_3$ Phosphonium iodide is used as a reducing agent, and in the preparation of organic phosphines Phosphonium chloride is dissociated at ordinary temperatures, but it can exist at 14° or under if under a pressure of 20 atmospheres It must therefore be preserved in sealed tubes, and prepared by the combination of phosphine with hydrogen chloride under pressure Similar remarks apply to phosphonium bromide, PH_4Br

Liquid hydrogen phosphide, P_2H_4 —When calcium phosphide, Ca_3P_2, is treated with water, and the gas evolved passed through a spiral tube in order to condense the water, and then through a U-tube immersed in a freezing mixture (pounded ice and salt), a colourless liquid is obtained which is spontaneously inflammable when exposed to the air The uncondensed gases which pass on are led into a trough of water in the fume closet, each bubble of gas as it comes in contact with the air may burn with a bright flash of light characteristic of crude phosphine This is due to the escape of some of the "liquid" phosphide The apparatus for the experiment is shown in Fig 219 The calcium phosphide is dropped through a wide tube into the Woulff's bottle containing water The liquid boils at 57° to 58° (735 mm) The empirical formula is PH_2 The vapour density is 75 5 (theory for P_2H_4 is 66) The molecular formula is therefore

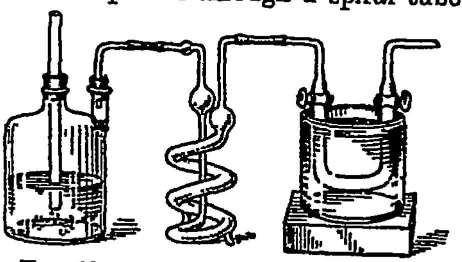


FIG 219 —The Preparation of Liquid Hydrogen Phosphide

P_2H_4, and if phosphorus be tervalent, the graphic formula is probably $H_2{=}P{-}P{=}H_2$, analogous with hydrazine N_2H_4

Solid hydrogen phosphide, $P_{12}H_6$ —When liquid hydrogen phosphide is exposed to light, or heated above its boiling point, it decomposes into gaseous phosphine, PH_3, and a solid phosphorus hydride with the empirical formula P_2H, thus $5P_2H_4 = 2P_2H + 6PH_3$ This solid is insoluble in water The same reaction takes place in the presence of hydrochloric or hydriodic acid which acts as catalytic agents The depression of the freezing point of a solution of the solid hydride in molten phosphorus corresponds with a molecular weight $P_{12}H_6$ When heated to 70° in a stream of carbon dioxide, it decomposes into phosphorus and hydrogen It takes fire when heated in air to 160°, and when heated *in vacuo* it evolves phosphine, forming a red substance also said to be a solid phosphorus hydride with the empirical formula P_9H_2 Prolonged heating is said to convert this hydride into red phosphorus There is some doubt about the real existence of the latter compound. It may be a solid solution of red phosphorus with one of the other hydrides, or with hydrogen

§ 6. Phosphorus Sulphides

Several compounds of sulphur and phosphorus have been reported They are all made by the direct combination of the two elements. The reaction between yellow phosphorus and sulphur is very violent, and red phosphorus is therefore used The sulphur also should be coarsely granulated in order to keep down the velocity of the reaction The mixture of sulphur and phosphorus is placed in a flask with a cork placed loosely in the neck The mixture is heated on a sand bath until the reaction starts, the flame is then removed This method of preparation is called Kekulé's process of preparing phosphorus sulphides By taking the right proportions of sulphur and phosphorus, the compounds P_4S_3, P_4S_7, and P_2S_5 can be made in this manner Several other sulphides have been reported, but some are in all probability mixtures.

Phosphorus pentasulphide, P_2S_5 —The crude sulphide made by Kekulé's process is distilled in a current of carbon dioxide A pale yellow crystalline mass is obtained which melts at 274° to 276°, and boils at 530° The vapour density 7 67 (air = 1) corresponds with $7\ 67 \times 28\ 9 = 221\ 7$ (oxygen=32) The theoretical value for P_4S_{10} is 224 ($O_2 = 32$) This sulphide is hydrolyzed by water $P_2S_5 + 8H_2O = 2PO(OH)_3 + 5H_2S$ It is used for replacing the oxygen in many hydroxyl compounds by sulphur Thus with water, as we have just seen, H—OH forms H—SH, and with alcohol, C_2H_5OH it forms ethyl mercaptan, C_2H_5SH With phosphorus pentachloride, PCl_5, it forms thiophosphoryl chloride, $PSCl_3$, a colourless liquid boiling at 125° This is the sulphur analogue of phosphoryl chloride

Phosphorus sesquisulphide, tetraphosphorus trisulphide, P_4S_3.—The crude sulphide prepared by Kekulé's process is a grey crystalline mass which can be purified by crystallization from solution in carbon disulphide or phosphorus trichloride, PCl_3, in the form of rhombic prisms, or the crude product can be purified by distillation *in vacuo* The vapour density of the sulphide corresponds with P_4S_3 It dissolves in alkaline sulphides, and is slowly attacked by water At 100° it inflames in air It melts at 172 5° to a reddish liquid which boils at 407° or 408°

§ 7 Matches

Common friction matches.—These are made by cutting soft wood into the required shape by machinery. One end of the strip is dipped into some inflammable substance—paraffin or sulphur, and then into a paste made from yellow phosphorus, manganese dioxide, glue, and colouring matter. The manganese dioxide may be replaced by other oxidizing agents—potassium chlorate, nitre, etc. The matches are then dried. The glue protects the phosphorus from oxidation, but by rubbing the head of the match on a rough surface, sufficient heat is generated to ignite the phosphorus in contact with the oxidizing agent. The burning phosphorus ignites the sulphur or paraffin, and this in turn fires the wood. Cotton threads dipped in paraffin are used in place of wood to form the so called *wax vestas*.

Safety matches.—In spite of the greatest care, the phosphorus disease prevails in match factories using yellow phosphorus. The substitution of red for yellow phosphorus is far less dangerous to the health of the worker. The head of the match is then made from a coloured mixture of antimony sulphide, potassium chlorate, and glue. Other oxidizing agents are used—red lead, potassium bichromate, etc. The surface on which the match is to be rubbed for ignition is covered with a mixture of red phosphorus, powdered glass, and glue. These matches—called safety matches—have the disadvantage that they can only be ignited by friction on a prepared surface or if quickly rubbed on a smooth non-conducting surface like glass or slate; but they are not liable to ignite by accidental friction.

Safety friction matches.—Matches can be made which strike on any surface by using Schenk's scarlet phosphorus, or phosphorus sesquisulphide—P_4S_3—in place of ordinary phosphorus. These matches are not so liable to accidental ignition as ordinary friction matches, and they are made without risk of phosphorus poisoning.

Questions

1. It is found that in 11.16 litres (calculated at 0° C. and 760 mm.) of any gaseous compound of phosphorus, there is never less than 15.5 grams of phosphorus present. Also that this volume of the vapour of phosphorus itself, under the same conditions, weighs 62 grams. State what conclusions may be drawn from the above data, with reference to the atomic and molecular weight of phosphorus.—*Cambridge Senior Locals.*

2. What volume changes occur where (i) sulphur is heated in nitrous oxide; (ii) Phosphorus is heated in nitric oxide; (iii) Sodium is heated in gaseous hydrogen chloride; (iv) Potassium is heated in gaseous ammonia? Give equations. What inferences can be drawn from the observed facts as to the formulæ of the bodies formed and destroyed?—*Owens Coll.*

3. Describe and explain the changes which take place when (*a*) sulphur, (*b*) phosphorus, (*c*) iodine, (*d*) zinc are severally boiled with concentrated potassium hydroxide solution.—*London Univ.*

4. Describe how from a specimen of calcium phosphate you would propose to make crystalline preparations of (*a*) calcium chloride, (*b*) ammonium magnesium phosphate. Give equations for the reactions involved.—*London Univ.*

5. What are the formula and name of the salt having the following percentage composition? Calcium, 38.72; phosphorus, 20.0; oxygen, 41.28.—*Glasgow Univ.*

6. Define the term "acid." In the light of your definition give reasons for assigning or refusing the name "acid" to aqueous solutions of the following: hydrogen sulphide, ordinary sodium phosphate, sodium bisulphate, copper sulphate, and alcohol (C_2H_5OH).—*Board of Educ.*

7. Describe the chlorides of phosphorus and give all the details essential for the preparation of a pure specimen of phosphorus pentachloride.—*Board of Educ.*

CHAPTER XXXI

THE OXIDES AND ACIDS OF PHOSPHORUS

§ 1 Phosphorus Pentoxide

WHEN phosphorus is burnt in an excess of air or oxygen, white clouds of phosphorus pentoxide condense as a voluminous powder Small quantities of other oxides of phosphorus may be formed at the same time which impart a slight garlic-like smell to the product Pure phosphorus pentoxide has no smell. The lower oxides of phosphorus present in commercial phosphorus pentoxide can be oxidized by re subliming the powder in a current of dry oxygen so that the mixture passes over warm platinized asbestos

Phosphorus pentoxide sublimes very slowly at 50°, but at 250° the sublimation is rapid The vapour density at 1400°, by V Meyer's process, corresponds with the molecular weight P_4O_{10}, but the simpler formula, P_2O_5, is generally employed for the sake of convenience. Phosphorus pentoxide can be melted by heating it quickly There are said to be three varieties crystalline, amorphous, and vitreous.

Phosphorus pentoxide is extremely hygroscopic, and it absorbs moisture from the air very quickly, hence its use for drying gases. When thrown into water, combination occurs with a hissing sound resembling the quenching of red hot iron, and metaphosphoric acid is formed $P_2O_5 + H_2O = 2HPO_3$ When this solution is boiled with water, or when the phosphorus pentoxide is thrown into hot water, orthophosphoric acid is formed $P_2O_5 + 3H_2O = 2H_3PO_4$ The heat of solution of the crystalline modification of phosphorus pentoxide is 41 Cals, of the amorphous powder, 34 Cals, of the vitreous variety, 29 Cals, and the product of combustion of phosphorus with oxygen has a heat of solution of 34 Cals The affinity of phosphorus pentoxide for moisture is so great that it can withdraw the elements of water from many organic and inorganic substances, *e.g* it converts nitric acid into nitrogen pentoxide, etc It resemble nitrogen pentoxide in constitution $O_2{\equiv}P{-}O{-}P{\equiv}O_2$, but this cannot apply to the molecule P_4O_{10} The corresponding acid—$P(OH)_5$—is not known, although the equivalent chloride, PCl_5, is known

§ 2 Orthophosphoric Acid and the Orthophosphates

Orthophosphoric acid, H_3PO_4, is formed when phosphorus pentoxide is dissolved in water, and the solution is boiled It is also formed when one part of red phosphorus is boiled with 16 parts of nitric acid, specific gravity 1 20,[1] in a flask fitted with a reflux condenser, and a ground glass

[1] A stronger acid may cause an explosion, and with a weaker acid the action is slow A trace of iodine will accelerate the action The nitric acid should be free from sulphuric acid

joint at the neck, as illustrated in Fig 220, so that the nitric acid which is volatilized may be returned to the flask When the phosphorus is all oxidized, the solution is evaporated to dryness, and the residue is finally heated in a platinum dish to a temperature not exceeding 180° to make sure all the nitric acid is driven off Orthophosphoric acid is also made by the action of sulphuric acid on bone ash as described for the manufacture of phosphorus.

Properties of orthophosphoric acid —By concentration *in vacuo*, or by heating to 140°, the acid can be obtained in six-sided prismatic crystals belonging to the rhombic system The acid melts at 42 3°, and dissolves readily in water It is tribasic—H_3PO_4—and it forms three series of salts—normal or tertiary, secondary, and primary according as all, two, or one of its hydrogen atoms are replaced by an equivalent radicle

	Primary	Secondary	Tertiary	Secondary
$\mathrm{HO}\\ \mathrm{HO}\\ \mathrm{HO}$ $\left.\right\rangle P{=}O$				

$$\left.\begin{array}{r}\mathrm{HO}\\\mathrm{HO}\\\mathrm{HO}\end{array}\right\rangle \mathrm{P{=}O}\qquad \left.\begin{array}{r}\mathrm{NaO}\\\mathrm{HO}\\\mathrm{HO}\end{array}\right\rangle \mathrm{P{=}O}\qquad \left.\begin{array}{r}\mathrm{NaO}\\\mathrm{NaO}\\\mathrm{HO}\end{array}\right\rangle \mathrm{P{=}O}\qquad \left.\begin{array}{r}\mathrm{NaO}\\\mathrm{NaO}\\\mathrm{NaO}\end{array}\right\rangle \mathrm{P{=}O}\qquad \left.\begin{array}{r}\mathrm{NaO}\\\mathrm{NH_4O}\\\mathrm{HO}\end{array}\right\rangle \mathrm{P{=}O}$$

Orthophosphoric acid — Sodium dihydrogen phosphate — Disodium hydrogen phosphate — Normal sodium phosphate — Microcosmic salt

The normal salt is alkaline to litmus, the secondary salt is neutral, and the primary salt is acid The hydrogen atom may be replaced by different radicles Thus the secondary acid salt—ammonium sodium hydrogen phosphate, also called microcosmic salt—is illustrated by the graphic formula above

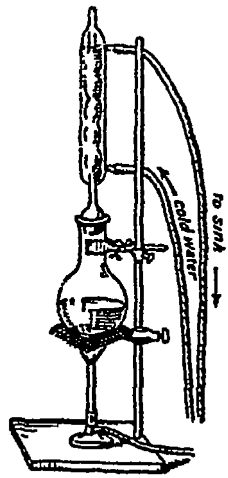


Fig 220 —Preparation of Orthophosphoric Acid

The constitution of phosphoric acid — The structural formula for phosphoric acid will depend upon what view is adopted about the valency of phosphorus—ter- or quinquevalent In the former case, we have

$$\mathrm{P}\left\langle\begin{array}{l}\mathrm{O{-}OH}\\\mathrm{OH}\\\mathrm{OH}\end{array}\right.\qquad\text{and}\qquad \mathrm{O{=}P}\left\langle\begin{array}{l}\mathrm{OH}\\\mathrm{OH}\\\mathrm{OH}\end{array}\right.$$

in the latter The oxychloride of phosphorus must be either

$$\mathrm{P}\left\langle\begin{array}{l}\mathrm{O{-}Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{array}\right.\qquad\text{or}\qquad \mathrm{O{=}P}\left\langle\begin{array}{l}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{array}\right.$$

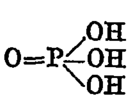
Phosphorus is undoubtedly quinquevalent in the pentafluoride and also in the pentachloride Accordingly, the latter formula is usually considered, without direct proof, to be the more probable, and hence it has been employed in what precedes Phosphoric acid is formed by treating the oxychloride, $O{=}PCl_3$, with water, and therefore $O{=}P{\equiv}(OH)_3$ is the most probable structural formula for phosphoric acid. With the notation discussed under periodic acid, "orthophosphoric acid" should be written $P(OH)_5$ but this acid and its salts are unknown The first dehydration product of $P(OH)_5$, stable at ordinary temperatures, is called orthophosphoric acid $O{=}P(OH)_3$, the corresponding chloride is $POCl_3$, phosphoryl chloride This is a convenient place to emphasize the fact

that compounds with the group O=P≡ are more stable than compounds with the group Cl_2=P≡ Phosphorus pentachloride, Cl_2=PCl_3, for instance, is readily dissociated by heat under conditions where O=PCl_3 is stable

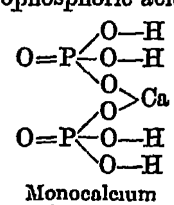
Sodium orthophosphates.—The disodium phosphate is the ordinary sodium phosphate used in the laboratory in testing for magnesium salts. It is obtained in the form of monoclinic prisms with 12 molecules of water of crystallization—$Na_2HPO_4.12H_2O$—by adding sodium carbonate to phosphoric acid until the solution is just alkaline, and evaporating the solution until it deposits crystals. The crystals effloresce in air, and melt at 35° The salt becomes anhydrous when heated, and 100 grams of water at 0° dissolve 2 5 grams of the salt, 82 grams, at 50°, and 99, at 100° If a mixed solution of sodium hydroxide and disodium phosphate be evaporated until the liquid crystallizes on cooling, hexagonal or rhombic crystals of the **normal sodium phosphate** separate with 12 molecules of water of crystallization—Na_3PO_4 $12H_2O$ Several other hydrates of this salt are known The aqueous solution of the normal phosphate is alkaline—probably owing to the reaction $H_2O + Na_3PO_4 \rightleftharpoons Na_2HPO_4 + NaOH$. If phosphoric acid be added to the disodium phosphate until the liquid gives no precipitate with barium chloride, the solution when evaporated gives crystals of **sodium dihydrogen phosphate**—H_2NaPO_4 H_2O The crystals are dimorphous, both forms belong to the rhombic system Aqueous solutions of this salt are acid If a mixture of, say, 6 grams of ammonium chloride, and 36 grams of the disodium phosphate be dissolved in as little hot water as possible, and the solutions be mixed, crystals of **sodium ammonium hydrogen phosphate, microcosmic salt** —$HNaNH_4PO_4$ $4H_2O$—will separate from the solution on cooling

Silver orthophosphate, Ag_3PO_4.—By mixing solutions of silver nitrate and sodium orthophosphate, a yellow precipitate of silver phosphate is obtained. The precipitate is soluble in nitric acid, and since nitric acid is produced during the precipitation of silver phosphate $3AgNO_3 + Na_2HPO_4 = Ag_3PO_4 + 2NaNO_3 + HNO_3$, the precipitation will be incomplete Silver phosphate also dissolves in aqueous ammonia.

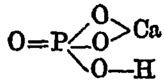
Calcium orthophosphates.—Calcium phosphate is one of the most important salts of phosphoric acid Pure crystalline tricalcium phosphate, $Ca_3(PO_4)_2$, has not yet been found in nature, or prepared in the laboratory The nearest approach to pure calcium phosphate is made by adding sodium phosphate to a solution of calcium chloride in the presence of ammonia. Calcined bones contain from 60 to 80 per cent of the normal phosphate Several more or less impure calcium phosphates occur in nature, see "the occurrence of phosphorus" The normal and the two acid phosphates are related to orthophosphoric acid as indicated in the following formulæ



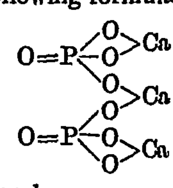
Orthophosphoric acid, H_3PO_4



Monocalcium phosphate, $Ca(H_2PO_4)_2$.



Dicalcium phosphate, $CaHPO_4$ or $Ca_2H_2(PO_4)_2$.



Tricalcium or normal phosphate, $Ca_3(PO_4)_2$.

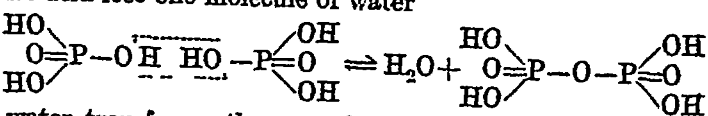
Normal calcium phosphate is very sparingly soluble in water 100 parts

of water dissolve about 0.003 part of the solid. The presence of alkalies decreases the solubility, while the presence of neutral salts—like sodium chloride, sodium nitrate—and acids—like carbon dioxide—increase its solubility in water. The dissolution of normal calcium phosphate in water—particularly in boiling water—is really a kind of hydrolysis, for a basic salt, $Ca(OH)_2.nCa_3(PO_4)_2$, is precipitated, and an acid salt remains in solution. Similar remarks apply to the action of water on the other calcium phosphates. The phosphates of magnesium, iron, and aluminium resemble calcium phosphate in their behaviour towards water. Calcium phosphate is converted into soluble acid salts or into soluble phosphoric acid when treated with concentrated nitric, hydrochloric, or sulphuric acid.

Vegetable life is mainly dependent upon the solubility of calcium phosphate in the soil solution for the phosphorus required for proper nutrition. To insure a quick distribution of the phosphate in soils, and a more concentrated solution of phosphoric acid in the water about the roots of plants for agricultural purposes, a more soluble phosphate than normal calcium phosphate is considered necessary. To convert the normal salt into a more soluble acid salt, normal calcium phosphate is treated with sulphuric acid—usually chamber acid—in order to transform most of it into the monocalcium phosphate: $Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$. The acid phosphate becomes $CaH_4(PO_4).H_2O$, and the calcium sulphate, $CaSO_4.2H_2O$. This mixture contains a little undecomposed normal phosphate. The mixture is generally called superphosphate, and sometimes "acid phosphate." The superphosphate is used as a fertilizer. On exposure to the air, moisture is absorbed, and the undecomposed normal phosphate reacts with the *soluble* monocalcium phosphate, forming a *sparingly soluble* dicalcium phosphate: $Ca_3(PO_4)_2 + CaH_4(PO_4)_2.H_2O + H_2O = 4CaHPO_4.2H_2O$. The superphosphate is then said to have "reverted" or "precipitated." The chief sources of the phosphatic fertilizers of commercial importance are (1) phosphatic rock; (2) bones and bone preparations; (3) guanos; (4) sewage, etc.—*e.g.* the littoral of the Red Sea; and (5) basic or Thomas slag. The latter is the discarded lining of basic process steel furnaces which absorbed phosphorus from pig iron in the process of manufacturing iron and steel. Sometimes crystals of tetracalcium phosphate—$Ca_4P_2O_9$, that is, $4CaO.P_2O_5$—are found in the slag.

§ 3. Pyrophosphoric and Metaphosphoric Acids

Pyrophosphoric acid, $H_4P_2O_7$, or $P_2O_3(OH)_4$.—This acid is formed when orthophosphoric acid is heated to 250°. *Two molecules of orthophosphoric acid lose one molecule of water*:



Boiling water transforms the pyrophosphoric acid back into the orthophosphoric acid. Pyrophosphoric acid is tetrabasic. The ethyl salt, $(C_2H_5)_4P_2O_7$, has a molecular weight corresponding with the tetrabasic acid when its effect on the boiling point of chloroform is measured. Sodium pyrophosphate is formed when the monohydrogen salt is calcined: $2Na_2HPO_4 = H_2O + Na_4P_2O_7$. Magnesium ammonium phosphate is readily transformed into magnesium pyrophosphate by calcination, as indicated

above $2(NH_4)MgPO_4 = Mg_2P_2O_7 + H_2O + 2NH_3$. The pyrophosphates are fairly stable salts, they pass into the orthophosphates when boiled with sulphuric acid Curiously enough, tetrabasic pyrophosphoric acid only forms quaternary or normal pyrophosphates, say $Na_4P_2O_7$, etc, and the secondary pyrophosphates, say $Na_2H_2P_2O_7$, etc The primary and tertiary salts are unknown Pyrophosphoryl chloride, $P_2O_3Cl_4$, corresponds with pyrophosphoric acid, $P_2O_3(OH)_4$

Magnesium ammonium phosphate, $Mg(NH_4)PO_4 \cdot 6H_2O$—This salt is obtained as a crystalline precipitate when a solution of a soluble phosphate is mixed with ammonia, ammonium chloride, and magnesium sulphate or chloride, and conversely, if ammonium phosphate be added to an ammoniacal solution of magnesium, the same salt is precipitated. These reactions are accordingly used for the determination of phosphorus, and of magnesium. When the precipitated magnesium ammonium phosphate is filtered, washed, and calcined, it is converted into magnesium pyrophosphate—$Mg_2P_2O_7$ The weight of the pyrophosphate enables the amount of phosphorus or of magnesium to be computed

Metaphosphoric acid, HPO_3—This acid is formed as a viscous solid when phosphorus pentoxide is left exposed to moist air, and it is also obtained by heating ammonium orthophosphate, or pyro or orthophosphoric acid to a red heat

$$\begin{matrix} HO \\ HO \\ HO \end{matrix}\!\!>\!P{=}O \rightleftharpoons H_2O + HO{-}P\!\!<\!\!\begin{matrix} O \\ O \end{matrix}$$

Metaphosphoric acid apparently bears the same relation to phosphorus that nitric acid bears to nitrogen Metaphosphoric acid is a transparent vitreous solid, sometimes called "glacial phosphoric acid" It fuses at 0°, and the commercial acid is usually cast in sticks It is readily soluble in water, and the solution slowly passes into the ortho acid, the change proceeds rapidly on boiling the solution Three polymers—HPO_3, $(HPO_3)_2$, and $(HPO_3)_3$—have been obtained

Vapour density determinations of the metaphosphoric acid prepared as indicated above, correspond with the formula $H_2P_2O_6$, and in consequence, the acid may be a dimetaphosphoric acid.

Consonant with the prefixes adopted for the periodic acids, $P(OH)_5$ should be called orthophosphoric acid, $PO(OH)_3$ mesophosphoric acid and $PO_2(OH)$ metaphosphoric acid Pyrophosphoric acid would then be dimesophosphoric acid The reason this acid is called "pyro" acid will be obvious from its mode of formation—Greek πυρ (pyr), fire

The metaphosphates—*Sodium metaphosphate*, $NaPO_3$, is formed by igniting either dihydrogen sodium phosphate, or hydrogen sodium ammonium phosphate, or dihydrogen sodium pyrophosphate Metaphosphoric acid is monobasic, and it forms a series of salts which may be regarded as derivatives of the hypothetical polymerized metaphosphoric acids. For instance

Acids	Salts
HPO_3, Monometaphosphoric acid	$NaPO_3$, Sodium metaphosphate
$(HPO_3)_2$, Dimetaphosphoric acid	$K_2P_2O_6$, Potassium dimetaphosphate
$(HPO_3)_3$, Trimetaphosphoric acid	$Na_3P_3O_9$, Sodium trimetaphosphate
$(HPO_3)_4$, Tetrametaphosphoric acid	$Pb_2P_4O_{12}$, Lead tetrametaphosphate
$(HPO_3)_5$, Pentametaphosphoric acid	$(NH_4)_5P_5O_{15}$, Ammonium pentametaphosphate
$(HPO_3)_6$, Hexametaphosphoric acid	$Na_6P_6O_{18}$, Sodium hexametaphosphate

There is some reason to doubt if many of the polyphosphates are anything more than mixtures of pyro and meta-phosphates

Distinguishing tests for the phosphoric acids.—The three phosphoric acids and their salts are distinguished by the difference in their behaviour towards silver nitrate, barium nitrate, and albumen

TABLE XLII —REACTIONS OF THE PHOSPHORIC ACIDS

	Orthophosphoric acid	*Pyrophosphoric* acid	*Metaphosphoric* acid
Silver nitrate	Canary yellow pp	White cryst pp	White gelatinous
Barium nitrate	No pp (if alkaline, white pp)	No pp (if alkaline white pp)	White precipitate
Albumen	Nil	Nil	Coagulated
Zinc acetate	*Nil*	*Insoluble pp*	*Nil*

All the phosphoric acids give a canary yellow precipitate with a large excess of a boiling solution of ammonium molybdate in nitric acid The precipitate is soluble in phosphoric acid, and a large excess of the molybdate solution is needed or no precipitate may be formed. The same result is obtained with all the acids of phosphorus since the nitric acid oxidizes them to phosphoric acid Arsenic oxyacids give a similar precipitate

When phosphorus pentoxide is treated with 30 per cent hydrogen peroxide, while cooled with ice-water, an acid—monoperphosphoric acid—resembling Caro's acid—possibly H_3PO_5—is obtained, with pyrophosphoric acid, crystals with the empirical formula $H_4P_2O_8$, diperphosphoric acid, or simply perphosphoric acid corresponding with persulphuric acid, are formed

History of the phosphoric acids—It was once thought that phosphoric acid existed in three isomeric forms (1) The ordinary acid which gave a yellow precipitate with silver nitrate (A S Marggraf, 1746), (2) the product obtained by heating the ordinary acid which gave a white precipitate with silver nitrate (T Clark, 1827), (3) the acid obtained by a thorough calcination of phosphoric acid and which gave a white precipitate with silver nitrate, and unlike the other two forms, coagulated a clear aqueous solution of albumen (J J Berzelius, 1816) Thomas Graham, 1833, proved that these three acids—which he called respectively ordinary, pyro- and metaphosphoric acids—were different modifications of phosphoric acid, and that they differed from one another by "the quantity of water combined with the acid" Graham also found that when the acids were saturated with a base, three series of phosphates were obtained, one series contained one equivalent of the base per equivalent of the acid, a second series contained two equivalents of the base, and a third series contained three equivalents of the base

§ 4 Phosphorous Oxide or Phosphorus Trioxide and Phosphorous Acid

Phosphorous oxide—P_4O_6—mixed with a large excess of phosphorus pentoxide, is formed when phosphorus is burnt in a limited supply of air,

Some red phosphorus and possibly a lower oxide of phosphorus are formed at the same time For this experiment, the phosphorus is placed in a glass tube, *A*, which is bent as shown in Fig 221, and fitted into one end of a long tube cooled by a jacket, *B*, containing water at 60° The cooled tube is fitted to a U tube, *C*, immersed in a freezing mixture, a plug of glass wool is placed in the condenser tube near the U-tube The phosphorus is ignited, and a slow stream of air is drawn through the apparatus by means of an aspirator connected to the U tube The phosphorus pentoxide is arrested by the glass wool, and phosphorus oxide passes into the U tube, where it is condensed into a white crystalline mass. The wash bottle, *E*, with concentrated sulphuric acid protects the product from moisture At the end of the experiment, the solid in the U tube can be melted and run into the bottle *D*

Properties—Phosphorous oxide so formed is a mass of monoclinic prisms, it melts at 22 5° to a waxy solid and boils at 173° The vapour density of the solid corresponds with the molecule P_4O_6, although the simpler formula, P_2O_3, is often used The lowering of the freezing points of solutions of phosphorous oxide in benzene correspond with a molecular weight of 227, and solutions in naphthalene, with a molecular weight 218. The theoretical value for P_4O_6 is 220 Phosphorous oxide smells like garlic and it is poisonous. When exposed to the air it is gradually oxidized to the pentoxide, and when placed in warm oxygen it bursts into flame It also ignites spontaneously in chlorine It is slowly attacked by cold water, forming phosphorous acid, H_3PO_3, and with hot water it forms red phosphorus, a lower oxide of phosphorus, and phosphine

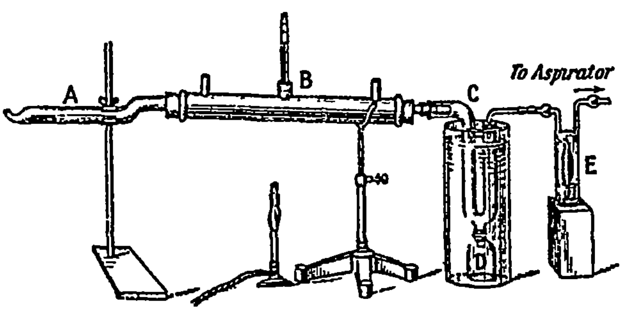


FIG 221—The Preparation of Phosphorus Trioxide—P_4O_6

Phosphorous acid, H_3PO_3—This acid is formed by the action of cold water upon phosphorous oxide $P_4O_6 + 6H_2O = 4H_3PO_3$, by the action of water on phosphorus trichloride $PCl_3 + 3H_2O = 3HCl + H_3PO_3$, or by passing a stream of chlorine through water beneath which phosphorus is melted The phosphorus trichloride formed in the latter reaction is at once decomposed by the water into phosphorous acid The solution is evaporated until the temperature has reached 180°, when, on cooling, it solidifies to a crystalline solid which melts at 70 1° When heated, phosphorous acid decomposes into phosphine and ortho phosphoric acid Phosphorous acid is a powerful reducing agent. It reduces silver nitrate to metallic silver, gold chloride to metallic gold, and copper sulphate to *metallic copper* It also absorbs oxygen, forming phosphoric acid Phosphorous acid is reduced by zinc and hydrochloric acid to phosphine $H_3PO_3 + 3Zn + 6HCl = 3ZnCl_2 + 3H_2O + PH_3$ The zinc and hydrochloric acid of course furnish nascent hydrogen

Constitution.—Phosphorous acid usually behaves as a dibasic acid, but a salt—sodium phosphite, Na_3PO_3—corresponding with a tribasic acid has been reported. Consequently, it is not possible to say definitely whether the formula of phosphorous acid should be written $P(OH)_3$, or $OPH(OH)_2$, since the evidence from different sources is contradictory. The formation of the acid from phosphorus trichloride points to the formula $P(OH)_3$, and the dibasicity of the acid to the formula, $O:PH(OH)_2$. The latter formula appears the more probable, and under special conditions the hydrogen directly attached to the phosphorus atom may have acidic properties, in the same way that the hydrogen of ammonia can be replaced by other radicles. Triethyl phosphite, $P(OC_2H_5)_3$, appears to be derived from a symmetrical tribasic phosphorous acid; though the scarcity of salts of the tribasic acid, and the existence of the unsymmetrical $O:PC_2H_5(OC_2H_5)_2$ show that two of the replaceable hydrogen atoms probably differ from the third. As in the case of sulphurous and nitrous acids, the facts are explained by assuming the desmotropic change

$$P\begin{matrix}\diagup OH\\ -OH\\ \diagdown OH\end{matrix} \rightleftharpoons O{=}P\begin{matrix}\diagup H\\ -OH\\ \diagdown OH\end{matrix}$$

As indicated previously, phosphorus may be both ter- and quinquevalent, but it is generally assumed that the properties of phosphorous acid correspond with quinquevalent phosphorus, and that the formula is $O:PH(OH)_2$.

The phosphites.—The salts of phosphorous acid—the phosphites—are soluble in water, and have an acid reaction. Solutions of phosphites give a precipitate with baryta and with lime water; they also precipitate metals from salts of silver, gold, and mercury.

Polyphosphorous acids.—A number of polyphosphorous acids—$H_4P_2O_5$, $H_5P_3O_7$, $H_7P_5O_{11}$—or rather salts corresponding with these acids, can be obtained by removing molecules of water from one or more molecules of the salts of phosphorous acid. These salts are analogous with the corresponding salts of phosphoric acid. Thus $P_2O_3 + 3H_2O = 2H_3PO_3$, or $P(OH)_3$—orthophosphorous acid; $P_2O_3 + 2H_2O = H_4P_2O_5$—pyrophosphorous and $P_2O_3+H_2O=2HPO_2$—metaphosphorous acid. The last-named acid is analogous with nitrous acid, HNO_2. Pyrophosphorous acid, $H_4P_2O_5$, is formed by the action of water on phosphorus trichloride, PCl_3, in the presence of hydrochloric acid: $2PCl_3 + 5H_2O = 6HCl + H_4P_2O_5$. The colourless crystalline mass melts at 38° and forms the ortho acid when treated with water. According to H. G. van de Stadt (1898), a metaphosphorous acid, HPO_2, corresponding with one molecule of H_3PO_3 less one molecule of water, is formed in white feathery crystals when phosphine slowly oxidizes under reduced pressure. It is said to be converted into phosphorous acid by the action of water vapour; and to melt at a higher temperature than phosphorous acid. There is some doubt whether this is really metaphosphorous acid.

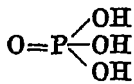
§ 5. Hypophosphorous Acid

Preparation.—When phosphorus is boiled with a solution of barium hydroxide, barium hypophosphite, $BaH_4P_2O_4$, is formed: $3Ba(OH)_2 + 8P + 6H_2O = 2PH_3 + 3BaH_4P_2O_4$. When this solution is treated with

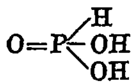
sulphuric acid, barium sulphate is precipitated. The clear aqueous solution is separated from the precipitate by filtration, and, when the solution is evaporated by gradually raising the temperature to 130°, it is sufficiently concentrated to deposit white crystals of the acid when cooled to 0°

Properties—The acid has the empirical formula H_3PO_2. The crystals melt at 25.4°. The acid is reduced by zinc and hydrochloric acid to phosphine. Hypophosphorous acid is a feeble monobasic acid which forms a series of salts called hypophosphites, where H_2PO_2 acts as a monad radicle. Thus, sodium hypophosphite, NaH_2PO_2 (p. 587), barium hypophosphite, $Ba(H_2PO_2)_2$, etc. The acid and its salts act as reducing agents, thus, with copper sulphate, a red precipitate of copper hydride, Cu_2H_2, is obtained. This shows that the reduction progresses a step further than is the case with phosphorous acid, and this reaction is one of the distinctive tests for hypophosphites. The acid and its salts also reduce salts of silver, gold, etc., to metals. The hypophosphites are oxidized to phosphates by oxidizing agents.

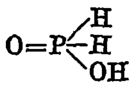
Constitution—Assuming the quinquevalency of phosphorus, the relations between phosphoric, phosphorous, and hypophosphorous acids are well illustrated by the graphic formulæ



Phosphoric acid
(Tribasic)

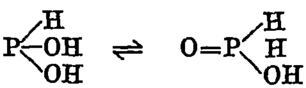


Phosphorous acid
(Dibasic)



Hypophosphorous acid
(Monobasic)

The last formula emphasizes the monobasicity of the hypophosphorous acid, although it is probable that one of the hydrogen atoms is labile corresponding with the desmotropic change



Dibasic inorganic hypophosphites are not known. The tendency of phosphorus to pass into the $O=P\equiv$ form is illustrated by the action of heat on this acid, and on its salts, for phosphoric acid and phosphine are produced: $2H_3PO_2 = OP(OH)_3 + PH_3$. Neither the anhydride nor the chloride corresponding with hypophosphorous acid is known.

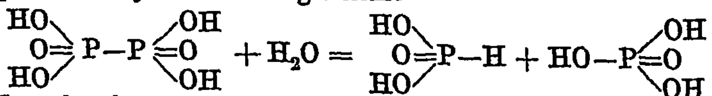
§ 6 Phosphorus Tetroxide. Hypophosphoric Acid

Phosphorus tetroxide, P_2O_4.—When phosphorus trioxide, P_4O_6, is heated in a sealed tube to about 440°, it decomposes into phosphorus tetroxide, P_2O_4, which appears as a crystalline sublimate in the sealed tube. The tetroxide reacts with water, *forming a mixture of phosphoric and phosphorous acids*: $P_2O_4 + 3H_2O = H_3PO_3 + H_3PO_4$. Phosphorus tetroxide is therefore to be regarded as a mixed anhydride which bears the same relation to phosphorus that nitrogen tetroxide, N_2O_4, bears to nitrogen. The latter, it will be remembered, forms nitrous and nitric acids with water.

Hypophosphoric acid, $H_4P_2O_6$, or H_2PO_3.—When phosphorus is exposed to a limited supply of moist air, a mixed solution of phosphoric, phosphorous, and hypophosphoric acids is formed. The solution is neutralized with sodium hydroxide, and a sparingly soluble sodium hypophosphate

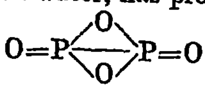
separates out A solution of this salt when treated with lead acetate gives an insoluble precipitate of lead hypophosphate, $PbPO_3$ This salt is filtered from the solution, and washed with hot water The precipitate is suspended in water, and a current of hydrogen sulphide passed through the solution Lead sulphide, PbS, is precipitated, and a solution of free hypophosphoric acid is obtained On evaporation, the excess of hydrogen sulphide is driven from the solution, but the evaporation cannot be carried very far without decomposing the acid Hence, the solution must be further evaporated in a desiccator *in vacuo* over sulphuric acid, Fig 79 In time, tabular, rhombic crystals of the hydrate $H_2PO_3 . H_2O$ separate The crystals melt at 62° Further desiccation of the crystals over sulphuric acid *in vacuo* gives the anhydrous acid, H_2PO_3, melting at 70° The acid is stable at ordinary temperatures, and is hydrolyzed by the mineral acids, forming a mixture of phosphoric and phosphorous acids The acid is dibasic, and the aqueous solution, unlike phosphorous acid, does not possess reducing qualities

Relation between hypophosphoric acid and phosphorus tetroxide —The fact that P_2O_4 furnishes phosphoric and phosphorous acids when treated with water is expressed by the structural formula $O{=}P{\equiv}O_3{\equiv}P$ If phosphorus tetroxide be the anhydride of hypophosphoric acid, we should expect $O{=}P{\equiv}O_3{\equiv}P + 2H_2O \rightarrow (OH)_2PO{-}O{-}P(OH)_2$ If the last formula really represents the structure of hypophosphoric acid, we should expect this acid to be a reducing agent like phosphorous acid, but it is not Its decomposition into phosphoric and phosphorous acids is well represented by the following scheme



Hypophosphoric acid Phosphorous acid Phosphoric acid

Accordingly, phosphorus tetroxide, which also decomposes into the same two acids in contact with cold water, has probably the structural formula



With two molecules of water, this gives hypophosphorous acid, and with three molecules of water a mixture of phosphoric and phosphorous acids Assuming that hypophosphoric acid (melting point 70°) corresponds with the above formula $(OH)_2OP{-}PO(OH)_2$, the hydrate (melting at 62°) is sometimes regarded as $(HO)_4P{-}P(OH)_4$ The molecular weight, deduced from the effect of the methyl salts, $(CH_3)_2PO_3$, and ethyl salts, $(C_2H_5)_2PO_3$, on the boiling points of methyl and ethyl iodides, corresponds with the formula H_2PO_3, not $H_4P_2O_6$ If the formula be H_2PO_3, phosphorus seems to act as a quadrivalent element in $O{=}P{=}(OH)_2$

Summary —To summarize, the more well-defined oxides and oxyacids of phosphorus are

Oxides	Acids
Phosphorous oxide, P_4O_6	Hypophosphorous acid, H_3PO_2
Phosphorus tetroxide, P_2O_4	Orthophosphorous acid, H_3PO_3
Phosphorus pentoxide, P_2O_5	Hypophosphoric acid, H_2PO_3
	Orthophosphoric acid, H_3PO_4
	Pyrophosphoric acid, $H_4P_2O_7$
	Metaphosphoric acid, HPO_3

Questions

1 How are phosphorus trioxide and phosphorus pentoxide respectively prepared? What happens when phosphorus pentoxide is dissolved in cold water and then the solution boiled? What is the action of heat on orthophosphoric acid?—*Aberdeen Univ*

2 Make the equation for the preparation of phosphine Compare phosphine and ammonia How may phosphorus be converted to phosphoric acid? Give equations —*Univ Pennsylvania, U S A*

3 What is the effect of heat on the following (*a*) phosphorous acid, (*b*) potassium chlorate, (*c*) lead nitrate (*d*) ammonium chloride?—*St Andrews Univ*

4 Give some examples of constitutional formulæ, and discuss the question of their use in chemical theory and investigation —*New Zealand Univ*

5 How may the different modifications of phosphoric acid be obtained, and by what tests may they be distinguished?—*Aberdeen Univ*

6 Phosphorous acid, H_3PO_3, has been variously represented as—

$$P\begin{cases}OH\\OH\\OH\end{cases} \qquad \text{and} \qquad O{=}P\begin{cases}H\\OH\\OH\end{cases}$$

Discuss the question indicating the significance of the following facts (1) That in most of its salts phosphorous acid is tribasic, (2) That an ether exists of the formula $PO_3(C_2H_5)_3$, (3) That phosphorous acid may be formed by the action of water upon phosphorus trichloride (4) That phosphenyl chloride, $C_6H_5PCl_2$ is formed by the action of the trichloride on benzene, C_6H_6, and that when the body is treated with water, $PO_2H_2(C_6H_5)$ is produced which on treatment with PCl_5 affords the following reaction $OPH(OH)C_6H_5 + 2PCl_5 = OPCl_2(C_6H_5) + POCl_3 + PCl_3 + 2HCl$ —*London Univ*

7 Give a brief account of the preparation isolation, and chief characters of the several oxides of phosphorus, and compare together the known oxides of nitrogen phosphorus, and arsenic —*London Univ*

8 Describe the preparation of phosphorus from bone ash; and give details, with a rough sketch of the apparatus you would employ, in order to convert this element into (*a*) phosphorus pentoxide (*b*) phosphine, (*c*) phosphorus trichloride (*d*) phosphonium iodide —*London Univ*

9 Give the names of the substances corresponding to the formulæ in the following equation—$P_4 + 3KOH + 3H_2O = PH_3 + 3KH_2PO_2$, and calculate the volume of gas at 21° and 780 mm pressure, and the weight of the salt which ought to be obtained by using 70 grams of phosphorus Why do we write P_4 and not $2P_2$? (H = 1, O = 16, P = 31, K = 39, one litre of hydrogen at 0° and 760 mm pressure weighs 0·09 gram)

10 Give an account of the preparation of orthophosphoric acid, show why it is considered to be a tribasic acid and also by a structural formula how it is related to pyrophosphoric acid —*London Univ*

11 State "the law of mass action" and illustrate it by the following examples (*a*) the action of water on antimony trichloride, (*b*) the action of steam on red hot iron

12 How is yellow phosphorus converted into the red variety and how can the reverse change be accomplished? What substances can be formed when phosphorus is (*a*) heated in air, (*b*) heated with nitric acid, and what is the relationship between them?—*Board of Educ*

13 Describe briefly the preparation of sodium hypophosphite from phosphorus Explain carefully the changes which occur when this salt is heated, and when solutions of mercuric chloride and acidified potassium permanganate, respectively, are mixed with its aqueous solution What is the basicity of hypophosphorous acid and how has it been ascertained?—*Board of Educ*

CHAPTER XXXII

Arsenic, Antimony, and Bismuth

§ 1 Arsenic—Occurrence, Preparation, and Properties.

Atomic weight, As = 74 96, molecular weight, As_4 = 299 84 Ter- and quinque valent Melting point, under pressure, about 817°, boiling point, 450°

Occurrence —The element occurs free, and combined in a great number of minerals—oxide, *arsenolite*, As_4O_6, sulphides, *realgar*, As_2S_2, *orpiment*, As_2S_3, *mispickel* or *arsenical pyrites* FeAsS, *cobaltite* or *cobalt glance*, CoAsS, arsenides—*tin white cobalt*, $CoAs_2$, *arsenical iron*, $FeAs_2$, and Fe_4As_3, *nickel glance*, NiAsS, *kupfernickel*, NiAs Arsenic also occurs in most samples of pyrites and hence it finds its way into sulphuric acid when sulphur dioxide is made by roasting pyrites Arsenic is also found in commercial zinc, and in the smoke from coal when the coal contains pyrites, hence also arsenic finds its way into the atmosphere of towns, where it can be detected, particularly in foggy weather Arsenic is also found in some mineral waters—*e g* Levico, Rocegno, etc A Gautier says that traces also occur normally in the human body The mere qualitative detection of arsenic does not therefore give much information unless the operation is more or less quantitative

Preparation —The element arsenic can be prepared by heating a mixture of the oxide, As_4O_6, with powdered charcoal in a clay crucible $As_4O_6 + 6C = 6CO + 4As$. The crucible is provided with a conical iron cap in which the arsenic sublimes Most of the commercial arsenic is either a natural product, or else it is made by heating mispickel in a clay tube fitted half its length with an inner sheet iron tube The arsenic sublimes into the iron tube By withdrawing and unrolling the tube, the element arsenic is obtained FeAsS = FeS + As The arsenic so obtained is not very pure It is purified by resublimation from a mixture of the crude element and charcoal

Properties —Ordinary arsenic is a steel-grey metallic-looking substance, which forms hexagonal rhombohedral crystals with a bright lustre It is called grey arsenic or γ-arsenic to distinguish it from two other allotropic modifications Grey arsenic is brittle, and, like the metals, it is a good conductor of heat Its specific gravity—5 727—is higher than typical non-metals In general physical properties grey arsenic resembles the metals, but otherwise it is classed with phosphorus among the non-metals. It sublimes very slowly at about 100°, and very rapidly at a dull red heat, without melting If heated under pressure, it melts about 817°, but under ordinary pressures it sublimes without melting The vapour

is lemon-yellow, and it smells like garlic. Arsenic is not altered by exposure to dry air but in moist air a surface film of oxide is formed At 180° it burns with a bluish flame, forming arsenious oxide, As_4O_6 It is readily oxidized by concentrated nitric and sulphuric acids. Dilute sulphuric acid has very little action on arsenic, while hot concentrated sulphuric acid dissolves arsenic forming sulphur dioxide and *probably* a very unstable arsenic sulphate, $As_2(SO_4)_3$, which immediately decomposes into the oxide Dilute nitric acid in the cold has very little action, but the hot acid oxidizes the element to arsenic acid—H_3AsO_4 Concentrated nitric acid and *aqua regia* also form arsenic acid Arsenic is not appreciably attacked by hydrochloric acid in the absence of air, but if air be present, it is slightly soluble As_4O_6 is said to be first formed and then dissolved as arsenic trichloride, $AsCl_3$ The element combines directly with chlorine at ordinary temperatures, forming arsenic trichloride Arsenic unites with almost all the metals, forming arsenides—*e g* iron—$FeAs_2$, cobalt—$CoAs_2$, nickel—NiAs, etc Arsenic is insoluble in sodium hydroxide

Allotropic modifications—When grey arsenic is quickly heated in a current of hydrogen, black glittering crystals of arsenic are deposited nearest the hot portion of the tube, and, further on, a yellow powder is deposited These are supposed to represent two allotropic modifications of arsenic The specific gravity of the black variety is 4 7, and of the yellow, 3 7 The yellow variety, called α-arsenic or **yellow arsenic**, is formed by the rapid condensation of arsenic vapour, and it is made by distilling arsenic in a current of carbon dioxide, and passing the vapour through a U-tube in which the arsenic is condensed by coming in contact with another stream of cold carbon dioxide, or through a U tube immersed in liquid air Yellow arsenic is soluble in carbon disulphide, from which it is deposited on evaporation in the form of rhombohedral crystals Yellow arsenic quickly passes into the grey variety when exposed to light The effect of yellow arsenic on the boiling and freezing point of carbon disulphide corresponds with the formula As_4 A reddish brown variety of arsenic is said to be deposited from carbon disulphide on long standing[1] The black modification of arsenic, called β-arsenic or **black arsenic**, is formed by the slow condensation of arsenic vapour It is either a black powder or a brittle glassy mass with a conchoidal fracture At 360° it passes into the grey variety

Atomic and molecular weights—Numerous analyses of arsenic compounds show that the atomic weight (O = 16) lies somewhere between 74 90 and 75 22 The best representative value is taken to be *74 96*, and the molecular weight of no known volatile compound of arsenic has less than 75 parts of arsenic per molecule when the molecular weight is determined by the vapour density (Avogadro's hypothesis) The specific heat of arsenic is 0 083 Hence by Dulong and Petit's rule, the atomic weight is nearly 6 4 ÷ 0 083 = 77 Arsenic in the arsenates is isomorphous with phosphorus in the phosphates, and the same value is obtained for the atomic weight by Mitscherlich's rule The vapour density of arsenic at about 860°, air = 1, is 10 2, and 5 45 at 1714°, and 5 37 at

[1] Arsenic suboxide, As_2O, is said to be formed together with some of the allotropic modifications of arsenic when the element is sublimed in open tubes There is some doubt about this

1736° The molecular weight at the high temperatures thus conforms with a two atom molecule and a molecular weight $5.4 \times 28.9 = 156$, and at low temperatures with a four-atom molecule

History —Arsenic was known to the ancients and considered by them to be a kind of sulphur Aristotle mentions a substance, σανδαράχη (sandarach), which appears to have been arsenic sulphide, and was called by Theophrastus ἀρσενικόν (arsenikon), meaning "potent" The element arsenic was prepared by Albertus Magnus, about 1250, and it was considered by the later alchemists to be a bastard or semi-metal Brandt first showed that "white arsenic" is the calx of arsenic, and since the establishing of Lavoisier's theory of oxidation, white arsenic has been considered to be the oxide of the element

Uses —Arsenic is used in the manufacture of arsenic compounds—arsenic trioxide, etc, and in certain alloys The presence of a trace in lead—1 1000—makes lead harder "Chilled shot" is hardened with arsenic The addition of arsenic lowers the melting point of the lead and increases its surface tension, so that when the shot is made by allowing the molten lead to drop from a height into water, the shot becomes spherical before it is cooled by the water

§ 2 Antimony—Occurrence, Preparation, and Properties

Atomic weight, Sb = 120 2, molecular weight, $Sb_4 = 480.8$ Ter-, quadri- and quinquevalent Melting point, 630 6°, boiling point over 1300°

Occurrence —Antimony occurs free in small quantities in Borneo and a few other places It is nearly always accompanied by some arsenic Antimony occurs combined with oxygen as *antimony bloom*, Sb_2O_3, and as *antimony ochre*, Sb_2O_4, combined with sulphur as *stibnite* or *grey antimony ore*, Sb_2S_3, and as *antimony blende* or *red antimony*, Sb_2S_2O It also occurs combined with sulphur and the metals

Preparation —Antimony is usually extracted from the native sulphides by heating the pulverized ore with scrap iron in a plumbago crucible. The iron combines with the sulphur forming a slag of iron sulphide which floats on the surface of the molten antimony $Sb_2S_3 + 3Fe = 2Sb + 3FeS$ In another process, the crude sulphide is melted in such a way that the molten sulphide flows away from the less fusible rocky impurities This process is called liquation The liquated sulphide is then mixed with about half its weight of charcoal and carefully roasted so as to convert the sulphide into oxide $2Sb_2S_3 + 9O_2 = 2Sb_2O_3 + 6SO_2$ Part of the antimony oxide condenses in the flues, and a residue of Sb_2O_4 and unchanged sulphide remains behind This is mixed with charcoal and sodium carbonate, and heated in a crucible The reactions are taken to be $Sb_2O_4 + 4C = 4CO + 2Sb$, and $3Na_2CO_3 + 6C + Sb_2S_3 = 9CO + 3Na_2S + 2Sb$ The antimony obtained by this process is subsequently refined by fusing it with a little nitre so as to oxidize the contaminating arsenic, lead, sulphur, etc

Properties —Antimony is a silvery-white solid with a high metallic lustre and a crystalline (rhombohedral) structure It is very brittle and can be easily pulverized Like the non-metals it is a poor conductor of heat, but it has a high specific gravity—6 7 to 6 8 From its physical properties, antimony, like arsenic, would be classed with the metals, but

its metallic characters are more pronounced than those of arsenic. Antimony melts at 629.2° in an atmosphere of carbon monoxide, and boils at 1440°. When the molten element is allowed to cool slowly and partially solidify in a crucible, the uncongealed portion may be poured off. The interior of the crucible is then lined with well formed rhombohedral crystals of antimony isomorphous with arsenic. In the act of solidification lead contracts, but antimony expands slightly. Hence molten mixtures of antimony with other metals when poured into moulds, take the fine and sharp impressions of the mould. The more important alloys of antimony are: *type metal*: lead, 75; tin, 5; antimony, 20. *Stereotype metal*: lead, 112; tin, 3; antimony, 18. *Britannia metal*: copper, 3; tin, 140; antimony, 7.

Antimony does not tarnish readily on exposure to dry air, but it is oxidized slowly by moist air. Antimony is used to cover other metals like brass and lead alloys. *Antimony black* is finely powdered antimony which is used to coat plaster casts, and make them imitate metals. When heated in air or oxygen, antimony burns with a bright bluish flame forming antimony trioxide, Sb_2O_3. Antimony combines directly with the halogens. The action is vigorous, and the combining element becomes incandescent. With chlorine, antimony trichloride, $SbCl_3$, is formed. Antimony also unites with sulphur, phosphorus, and arsenic, forming sulphides, phosphides, and arsenides respectively. Dilute hydrochloric and sulphuric acids have little or no action upon antimony, but the more concentrated acids respectively form chloride: $2Sb + 6HCl = 2SbCl_3 + 3H_2$; and an unstable antimony sulphate: $2Sb + 6H_2SO_4 = 6H_2O + 3SO_2 + Sb_2(SO_4)_3$. Antimony thus behaves towards these acids like a typical metal. Dilute nitric acid has scarcely any action, but it probably forms an unstable antimony nitrate, $Sb(NO_3)_3$. Concentrated nitric acid does not dissolve the metal but rather oxidizes it to insoluble Sb_2O_3 or Sb_2O_5, or a mixture of Sb_2O_4 and Sb_2O_5.

Allotropic modifications.—Like phosphorus and arsenic, antimony exhibits allotropism. The variety now under discussion is called common or rhombohedral or β-antimony. Yellow or α-antimony is formed when antimony hydride gas, SbH_3, is treated with air at $-90°$: $4SbH_3 + 3O_2 = 4Sb + 6H_2O$. This passes into black antimony on exposure to light. If a current of electricity be passed through a solution of antimony trichloride in hydrochloric acid—using an antimony anode, and a platinum cathode—an amorphous powder of specific gravity 5.78 is deposited on the cathode. The cathode has then the appearance of a smooth polished graphite rod. The deposit appears to be a solid solution of antimony trichloride in antimony. If this deposit be rubbed or scratched, an explosion occurs. This is attended with the transformation of this form of antimony into the stable rhombohedral variety; at the same time the temperature rises to about 250°. Clouds of antimony trichloride are given off at the same time. Hence the term explosive antimony is applied to the solid solution of the trihalide in a antimony. A similar substance is said to be made by the rapid cooling of antimony vapour. Under these conditions, an amorphous black powder is obtained with a specific gravity 5.3. This variety slowly passes into rhombohedral antimony at 100° and rapidly at 400°.

Atomic and molecular weights.—The many analyses of antimony compounds show that the atomic weight of this element (oxygen = 16) lies

somewhere between 119 79 and 122 53, the best representative value is considered to be 120 2 The molecular weight of all known volatile compounds of antimony show that this number is the smallest weight of that element which enters into the composition of any one of its molecules The vapour density of antimony at 2000° corresponds with the one-atom molecule; at 1640° very nearly with a two-atom molecule, and at 1440° very nearly with the molecule Sb_3 By analogy with arsenic and phosphorus, the latter number probably means that the vapour contains a mixture of Sb_4 and Sb_2 molecules. According to Dulong and Petit's rule, since the specific heat of antimony varies from 0 046 at 186° to 0 0537 at 300°, the approximate atomic weight of antimony varies from $6\,4 - 0\,046 = 139$, to $6\,4 - 0\,0537 = 119$. This agrees with the atomic weight 120 2

History—Stibnite or antimony sulphide has long been employed by the women of the East as a medicine, and as an article of toilet for darkening the eyebrows It is mentioned in this connection in the Old Testament (2 Kings, ix 30, Ezekiel, xxiii 40) Pliny terms it *stibium*, and in a Latin translation of Geber, it is called *antimonium* Both terms were in common use [1] up to the time of Lavoisier for antimony sulphide The latter term is supposed to be derived from the Greek ἀντι (anti), against, μονος (monos), one, or French *moine*, a monk At the end of the eighteenth century, the properties of antimony had probably been investigated more carefully than the properties of any other element The preparation of the element, and the known and imagined properties of antimony were described by Basil Valentine—a Benedictine monk of South Germany—about the fourteenth century In his book entitled *Triumph-Wagen des Antimonii* (The Triumphant Chariot of Antimony), Valentine approaches the subject with awed devotion "He who would write of antimony needs a great consideration and a most ample mind In a word, one man's life is too short to be perfectly acquainted with all its mysteries" The same remark might be applied with equal force to any one of the elements.

§ 3 Bismuth—Occurrence, Preparation, and Properties

Atomic weight, $Bi = 208$, molecular weight, $Bi_2 = 416$ Ter-, quadri, and quinquevalent Melting point, 269°, boiling point, 1435°

Occurrence—Bismuth is found in many localities in a fairly pure condition in a free state It also occurs combined with sulphur as *bismuth glance*, Bi_2S_3, with tellurium as *tetradymite*, Bi_2Te_3, and with oxygen as *bismite bismuth ochre*, Bi_2O_3 *Bismuthite* is a hydrated carbonate

Preparation—Bismuth is isolated by roasting the sulphide so as to form the oxide, Bi_2O_3 $2Bi_2S_3 + 9O_2 = 2Bi_2O_3 + 6SO_2$ The oxide is reduced to the metal by heating it with charcoal If the metal is to be refined, it is fused on an inclined plate so that the impurities are oxidized

Properties—Bismuth is a greyish-white solid resembling antimony, but it has also a faint reddish tinge Bismuth is hard, brittle, lustrous,

[1] Native antimony sulphide was called "kohl" by the Arabians, and later the name was changed to "alkol," and later still into "alkohol" In the Middle Ages, this latter term was applied to almost any fine powder produced by trituration or sublimation, and later, distillation The term "alcohol," at later periods, was gradually confined to "spirits of wine" produced by distillation.

crystalline, and like antimony, expands slightly in passing from the liquid to the solid condition The metallic qualities of bismuth are far more pronounced than is the case with antimony and arsenic In arsenic, the non-metallic properties predominate, in bismuth, the metallic qualities preponderate. Antimony is intermediate between bismuth and arsenic Bismuth melts at 269° If the molten metal be allowed to partly solidify in a crucible, and the uncongealed fluid be poured off, the crucible will be found lined with rhombohedral crystals of the element Bismuth boils at 1420°, and it distils in an atmosphere of hydrogen if heated over 1100° Bismuth oxidizes superficially on exposure to air, but if heated in air, it burns, forming Bi_2O_3 Bismuth decomposes steam at a red heat, but it is not affected by cold air free water It unites directly with the halogens It does not form a hydrogen compound, whereas antimony and arsenic form trihydrides Bismuth is but slightly attacked by hydrochloric acid—hot or cold, dilute or concentrated, it is very sparingly soluble in hot sulphuric acid forming bismuth sulphate, $Bi_2(SO_4)_3$, and sulphur dioxide Bismuth is readily attacked by dilute and concentrated nitric acid forming bismuth nitrate, $Bi(NO_3)_3$, which dissolves in aqua regia forming bismuth chloride, $BiCl_3$ Thus, nitric acid with bismuth gives a soluble nitrate, with antimony an insoluble oxide, and with arsenic, a soluble oxyacid

Atomic and molecular weights.—The atomic weight of bismuth, oxygen = 16, lies between 207 9 and 210 8, the best representative value is taken as 208, and the atomic weight deducted from Dulong and Petit's rule, when the specific heat of bismuth at 18° is 0 0303, and 6 4 — 0 0303 = 211 Hence, 208 is taken to represent the atomic weight of bismuth The vapour density of bismuth between 1600° and 1700° corresponds with a mixture of molecules of Bi and Bi_2, and at 2000° the molecule is monatomic

Uses.—Bismuth is used in the manufacture of alloys. The bismuth alloys are usually somewhat hard, and fusible Many of the "fusible alloys" melt in warm water For instance, *Newton's metal* (tin, 3, lead, 5, bismuth, 8) melts at 94 5°, *Rose's fusible metal* (tin, 1, lead, 1, bismuth, 2) melts at 93 75°, and *Wood's fusible metal* (tin, 1, lead, 2, cadmium, 1, bismuth, 4) melts at 60 5° Fusible alloys, which melt at a low temperature, are used for making safety plugs in steam boilers, fuses in electrical connections, in fire alarms, and in automatic sprinklers for buildings so that if a fire breaks out, the heat fuses a plug of the water pipe and thus allows a rush of water from the main The gas pipe which enters a building can be fitted with a piece of fusible alloy so that if a fire breaks out, the alloy will melt, choke the gas pipe, and stop the flow of gas. Fireproof doors can also be kept open by fusible plugs which allow the doors to automatically close in the event of fire

History.—Metallic bismuth, called marcasite,[1] was first described by Basil Valentine in the fourteenth century, and it was later classed by Paracelsus as a bastard metal Agricola considered it to be a true metal Some of the early writers confused bismuth with antimony (A. Libavius) and with zinc (N Lemery) J H Pott (1739) first demonstrated the

[1] The term marcasite was formerly employed somewhat vaguely for any ore with a metallic appearance, and especially to ores now classed as pyrites The term is now confined to a special variety of iron pyrites (*q v*)

characteristic properties of bismuth, and its reactions were later studied by S F Geoffroy (1753), and by T Bergmann (1780) The name bismuth is supposed to be derived from the German "Weissmuth," white matter.

§ 4 Arsenic and Antimony Hydrides.

Preparation—Bismuth does not form a hydride The hydrides of arsenic—arsine, AsH_3—and of antimony—stibine, SbH_3—resemble phosphine and ammonia in composition and many properties Neither arsenic nor antimony unite directly with hydrogen Both hydrides are produced by the action of nascent hydrogen from metallic zinc or magnesium and sulphuric acid, upon solutions containing compounds of these two elements Arsine is, and stibine is not, produced by the action of hydrogen generated when potassium hydroxide acts upon zinc Fleitmann's test (1850) for the distinction of arsenic and antimony is based upon this fact When arsine or stibine is prepared by the action of nascent hydrogen upon an arsenic or an antimony salt, in an apparatus similar to that used for the preparation of hydrogen, the gas is accompanied by much hydrogen Arsine practically free from hydrogen is made by the action of dilute sulphuric acid upon sodium arsenide or on zinc arsenide, Zn_3As_2 $Zn_3As_2 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4$ Stibine is best made by the action of dilute sulphuric acid upon an alloy of antimony and zinc, or calcium, or magnesium [1] The gas is passed through a U-tube immersed in liquid air The stibine condenses to a white solid, and the hydrogen passes on When the U-tube is removed from the liquid air, the stibine vaporizes.

Properties—Both gases are very poisonous. One bubble of arsine is said to have produced fatal effects. Gehlen lost his life with this gas in 1815 Stibine is less stable than arsine Both gases when passed through a hot tube deposit the elements in the form of a metallic film Both gases burn with a blue flame which give metallic films in contact with cold porcelain Arsine gives arsenious oxide, As_2O_3, on combustion, stibine, Sb_2O_3 Stibine explodes when electric sparks are passed through the gas, arsine decomposes with the deposition of arsenic Arsine can be exploded with fulminating mercury Both compounds are endothermal $As + 3H = AsH_3 - 36\ 7$ Cals, and $Sb + 3H = SbH_3 - 81\ 8$ Cals When an endothermal compound decomposes, heat is evolved. If such a compound begins to decompose at any point of its mass, the surrounding molecules are heated, and they too are decomposed developing more heat The decomposition may thus traverse the whole mass if a vigorous enough impulse be imparted for the decomposition of a sufficient number of molecules to raise the temperature of the surrounding molecules to the temperature of decomposition Arsine liquefies at −55°, and solidifies at −119°, stibine liquefies at −18°, and solidifies at −88°

Composition—The composition of arsine or stibine can be determined by passing electric sparks through the gas arsenic or antimony is deposited, and three volumes of hydrogen are formed. *E g*

$$\underset{2\text{ vols}}{2AsH_3} = \underset{\text{Solid}}{2As} + \underset{3\text{ vols}}{3H_2}$$

[1] Zinc arsenide is made by heating metallic zinc and arsenic in a closed crucible so as to melt the mass The calcium antimonide is made by fusing antimony, calcium chloride, and sodium in an iron crucible The other antimonides are prepared in a similar manner

If, say, arsine be passed over hot weighed copper oxide and the resulting water and copper arsenide are weighed, every one part by weight of hydrogen corresponds with 24.987 grams of arsenic. The atomic weight of arsenic by a previous experiment is 74.96. Hence, the formula for arsine is $(AsH_3)_n$ where n is to be determined; similarly, the formula of stibine is $(SbH_3)_n$. But, the vapour density of arsine, hydrogen = 1, is 77.9, and of stibine, 123.6. These numbers correspond with the formulæ AsH_3 and SbH_3.

Action on silver nitrate.—The two gases, arsine and stibine, are distinguished by their behaviour towards solutions of silver nitrate. With *concentrated* silver nitrate solutions, arsine gives a yellow compound of silver arsenide and silver nitrate: $AsH_3 + 6AgNO_3 = AsAg_3.3AgNO_3 + 3HNO_3$. This compound is decomposed by water forming metallic silver and arsenious acid: $AsAg_3.3AgNO_3 + 3H_2O = 6Ag + 3HNO_3 + H_3AsO_3$. This is the principle of H. Gutzeit's test (1879). If a *dilute* solution of silver nitrate be used, silver is at once precipitated, A. W. Hofmann's test (1860): $AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + 6HNO_3 + H_3AsO_3$. Stibine under similar conditions forms a precipitate of silver antimonide, Ag_3Sb, contaminated with some metallic silver formed during the action of the hydrogen on the nitric acid. This reaction serves to distinguish and separate arsenic from antimony. The difference in the two reactions depends upon the fact that arsine is oxidized to arsenious acid more readily than the stibine, and thus arsine, like phosphine, acts as a reducing agent.

Marsh's test.—The underlying principle of the following test for arsenic was devised by J. Marsh in 1836. Place about 3 grams of metallic zinc in a small flask *A*, Fig. 222, and add 20 c.c. of sulphuric acid (1 volume of acid, 8 volumes of water). The exit tube is fitted with a calcium chloride drying tube, *E*. When all the air has been expelled from the apparatus by the hydrogen, light the jet of gas issuing from the exit tube *B*. Light the gas burner so that the exit tube is heated at *C*. If no mirror is formed in the tube near *C*, the reagents are free from arsenic and antimony. Recharge the apparatus, and add the solution to be tested *via* the tap funnel *D*. If arsenic or antimony be present, a mirror will be deposited in the tube in 15 or 20 minutes. The gas is then extinguished and the exit tube disconnected. The mirror can be tested for arsenic by heating the mirror with a small flame while the tube is held in an inclined position. A garlic-like odour can be detected if 0.01 milligram of arsenic is present. When the tube is cold arsenic trioxide will be found at a little distance from the flame in octahedral crystals which can be seen with the naked eye. These three results—mirror, garlic-like odour, and octahedral crystals—prove the presence of arsenic. Cumulative evidence is furnished by the application of other tests. If antimony be present, the mirror will be found nearer the hot flame *C* than is the case with arsenic; indeed, some antimony may be deposited in the tube before the gas reaches the hottest portion of the tube because stibine is more readily decomposed than arsine. If the exit tube be not heated at *C*, and the gases be burned

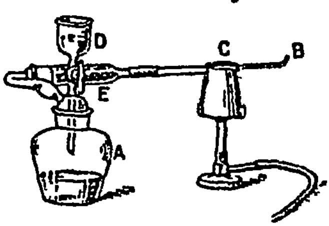


FIG. 222.—Modified Marsh's Apparatus.

with hydrogen at the end of the tube, a piece of glazed porcelain held in the flame will receive a steel grey or black deposit of arsenic or a velvety brown or black deposit of antimony If the deposit be treated with sodium hypochlorite solution, arsenic dissolves, while antimony remains insoluble. This illustrates the more ready oxidizability of arsenic than antimony

Antimony forms but one hydride with hydrogen, SbH_3, arsenic forms a second hydride—arsenic dihydride—supposed to be As_2H_2 This is the velvety-brown powder deposited when arsine is partially oxidized, when a jet of burning arsine impinges on porcelain, and when water is electrolyzed with an arsenic cathode The corresponding compounds of phosphorus and nitrogen are unknown Cacodyl, $As_2(CH_3)_4$, is the only compound of arsenic analogous with P_2H_4, and with hydrazine, N_2H_4

§ 5 Halogen Compounds of Arsenic, Antimony, and Bismuth

Arsenic trichloride, $AsCl_3$, is formed by the direct union of the elements when arsenic is brought in contact with chlorine, and it is also formed by distilling a mixture of arsenic trioxide with hydrochloric acid The distillate of arsenic trichloride is a heavy, colourless, viscid liquid, boiling at 132° The liquid freezes to white needle-like crystals at −18° The mode of formation of arsenic trichloride $As_4O_6 + 12HCl \rightleftharpoons 4AsCl_3 + 6H_2O$ suggests that arsenic trichloride is a salt and arsenious oxide a base The basic properties of arsenious oxide are feeble as is shown by the hydrolysis of the trichloride in contact with water With water, arsenic trichloride forms arsenic oxychloride, $AsCl(OH)_2$ or $AsOCl$, with boiling water, arsenious acid is formed $AsCl_3 + 3H_2O \rightleftharpoons H_3AsO_3 + 3HCl$, and the arsenious acid decomposes with the separation of arsenious oxide, As_4O_6 There is some doubt if arsenic pentachloride, $AsCl_5$, is formed, when arsenic trichloride is cooled with an excess of chlorine Some consider the alleged arsenic pentachloride is a solution of chlorine in arsenic trichloride The pentachloride, if formed, decomposes at −28° $AsCl_5 \rightleftharpoons AsCl_3 + Cl_2$ Arsenic trifluoride, AsF_3, is formed as a volatile fuming liquid boiling at 63° when arsenious oxide, As_4O_6, is distilled with the materials—calcium fluoride and sulphuric acid—used to generate hydrofluoric acid. Arsenic trifluoride is decomposed by water with the formation of hydrofluoric acid Arsenic pentafluoride, AsF_5, is known. Arsenic tribromide is a liquid which gives colourless prisms when cooled, arsenic triiodide forms orange-red rhombohedral crystals These compounds are formed by the direct union of the elements Arsenic pentiodide, AsI_5, and also the iodides AsI and As_2I_4 (or AsI_2) have been reported the first named is very doubtful.

Antimony trichloride, $SbCl_3$, is formed by the action of dry chlorine on an excess of antimony, and also by the distillation of an intimate mixture of antimony or stibnite with mercuric chloride It forms colourless crystals melting at 73°, and boiling at 223° The vapour density 225 4 corresponds with the formula $SbCl_3$ "Butter of antimony" is a viscid mass formed by the action of hydrochloric acid on stibnite When chlorine is passed through fused antimony trichloride, antimony pentachloride, $SbCl_5$, is formed as a colourless or slightly yellow liquid which crystallizes at −6° fumes in air, and boils with partial dissociation into

antimony trichloride and chlorine at 140°. Antimony pentachloride thus resembles phosphorus pentachloride: $SbCl_5 = SbCl_3 + Cl_2$. Antimony trichloride is decomposed by water forming the antimony oxychloride as a white precipitate. The composition of the oxychloride depends upon the amount and temperature of the water. Thus, with one part of antimony trichloride and 1.7 parts of water at ordinary temperatures, a precipitate of SbOCl is formed; with 5 to 50 parts of water, a precipitate of $2SbOCl.Sb_2O_3$ is formed; and by boiling with an excess of water, Sb_2O_3 is precipitated. The oxychloride was once used in medicine under the name "powder of Algaroth"—after V. Algarotus. Antimony also forms crystalline trifluoride, triiodide, and tribromide by the direct action of the proper elements on one another.

Bismuth trichloride, $BiCl_3$, is formed by the direct action of chlorine on bismuth; by heating bismuth with mercuric chloride; and by the action of *aqua regia* on bismuth. Bismuth trichloride is a white crystalline mass, deliquescent in air. It melts at 227° and boils at 428°. Its vapour density 328 corresponds with the formula $BiCl_3$. Unlike arsenic and antimony oxychlorides, bismuth oxychloride, BiOCl, is not decomposed by water. When bismuth trichloride is dissolved in a little water it forms a syrupy liquid, but with an excess of water a white precipitate of bismuth oxychloride, BiOCl. The dried precipitate is sometimes called "pearl white," and used as a white pigment. Bismuth oxychloride is insoluble, and antimony oxychloride is soluble in tartaric acid. Bismuth tribromide, $BiBr_3$, is an orange yellow solid; bismuth triiodide, BiI_3, a reddish brown powder; and bismuth trifluoride, BiF_3, a white solid. These compounds are prepared in a similar manner to the trichloride. They too give precipitates of the basic salts with water. Bismuth triiodide unites directly with hydrogen iodide forming a monobasic acid—$HBiI_4.4H_2O$ called hydr-iodo-bismuthous acid. The potassium iodobismuthite, $KBiI_4$, crystallizes in red plates.

§ 6 Arsenic Trioxide, Arsenious Acids

The molecule of arsenic trioxide or arsenious oxide is symbolized As_4O_6, although usually written As_2O_3. This is perhaps the most important compound of arsenic, and in commerce it is often called "white arsenic," or simply "arsenic."[1] Small quantities occur free in nature. Arsenic trioxide is formed by oxidizing arsenic with nitric acid and by the combustion of arsenic. Unlike phosphorus, the oxidation of burning arsenic stops when the trioxide is formed; phosphorus passes a stage further and forms the pentoxide. Commercial "white arsenic" is a by-product in the roasting of arsenical ores; the arsenic is oxidized to the trioxide and the fumes are led through a series of chambers or flues arranged to present an extended condensing surface to the gases. The crude product—"arsenical soot"—is collected periodically. It is refined by sublimation from iron cylinders.

Properties.—Like phosphorous oxide, arsenious oxide occurs in several different forms. Amorphous arsenic trioxide, or vitreous arsenic is a

[1] A little known arsenic suboxide, As_2O, is said to be formed together with allotropic modifications of the element when metallic arsenic is sublimed in an open tube.

colourless, non-crystalline, glassy substance produced when the vapour of arsenic trioxide is *slowly* condensed at a temperature slightly below its vaporizing temperature It melts at about 200° and volatilizes at 218°. 100 parts of water at 10° dissolve 3 67 parts of vitreous arsenic oxide in 6 hours, the solubility diminishes on standing *E g* after standing 1 day, the solubility fell to 3 31, 21 days, 1 71, and 2¼ years, 1 71 Vitreous arsenic trioxide can be preserved unchanged in a sealed tube, but if it be exposed to the air it gradually becomes opaque and forms crystals of octahedral arsenic trioxide belonging to the cubic system Similar crystals are produced when the vapour of arsenic trioxide is *rapidly* condensed, and when aqueous or hydrochloric acid solutions of the trioxide are allowed to crystallize Octahedral arsenic trioxide has less than one-third the solubility of the vitreous variety The specific gravity of the vitreous compound is 3 74, and of the octahedral form, 3 63 The passage from the vitreous to the octahedral variety is attended by an evolution of heat, 5 3 Cals Octahedral arsenic trioxide vaporizes without fusion, but if heated under pressure it melts and forms the vitreous variety If a hot saturated solution of arsenic trioxide in potassium hydroxide be cooled, prismatic needle-like crystals of rhombic arsenic trioxide separate The latter are sometimes said to belong to the monoclinic system—see "Antimony Trioxide" This variety is also formed when either of the preceding forms of arsenic trioxide are heated for a long time at 200° Its specific gravity is 4 15 If the lower part of a sealed tube containing arsenic trioxide be heated above 400°, the lower part will contain vitreous, the middle prismatic (rhombic), and the upper part octahedral (cubic) arsenic trioxide This experiment is due to H Debray (1864) A mixture of the prismatic and octahedral crystals will be found in the zone between the octahedral and prismatic crystals Fig. 223 will give some idea of the crystals in the intermediate zone as they appear magnified under a 1½" objective The vitreous form is the unstable variety, and the octahedral form the stable variety at ordinary temperatures The vitreous variety can exist at ordinary temperatures because of the slow speed of transformation into the octahedral form At 100° the speed is quite fast At higher temperatures still, the octahedral form passes into the monoclinic variety

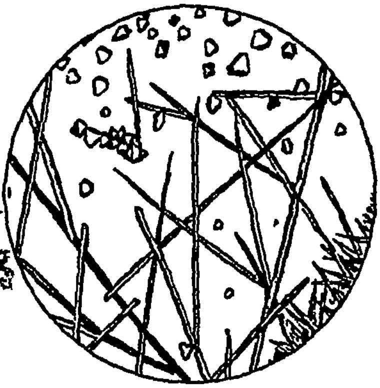


FIG 223—Dimorphism of Arsenic Trioxide

All three varieties of arsenic trioxide vaporize at 218° The vapour density between 500° and 800° corresponds with the molecule As_4O_6, and at 1732°, with As_2O_3 Arsenic trioxide is quite stable if heated in air or oxygen at 100° Strong oxidizing agents—like iodine, hydrogen peroxide, nitric acid, and ozone—transform it into arsenic acid Arsenic trioxide dissolves in hydrochloric acid *forming* arsenic trichloride Reducing agents—stannous chloride—transform it into arsenic and arsine Arsenic trioxide is very poisonous—0 06 gram is near the fatal dose for an ordinary man, but the habitual use of small doses makes the system

more or less immune to the effects of much larger quantities.[1] The antidote is freshly precipitated ferric hydroxide made by adding aqueous ammonia to a ferric salt—e.g. ferric chloride The efficacy of the antidote depends on the formation of an insoluble compound with iron hydroxide

Uses—Arsenic trioxide is used in the manufacture of pigments—*Scheele's green*, for instance, is a copper hydrogen arsenite, $HCuAsO_3$, once largely used to colour wall paper; *Paris green* or *Schweinfurt green* is a double salt of copper acetate and copper metaarsenite—$3Cu(AsO_2)_2 . Cu(C_2H_3O_2)_2$ It is used as insecticide, and for poisoning vermin Arsenic trioxide is also used in preserving the skins of animals, and in the manufacture of glass and opaque enamels

Arsenites—Aqueous solutions of arsenious oxide exhibit a feebly acid reaction, and redden blue litmus, probably due to the formation of an unstable arsenious acid, H_3AsO_3 This acid has never been isolated because the solution, on concentration, deposits crystals of the trioxide Salts corresponding to ortho-, pyro-, and meta-arsenious acid are known The constitution of the salts of these three acids may be understood from the graphic formulæ

Ortho arsenious acid	Pyro arsenious acid	Meta arsenious acid
$HO{-}As{<}^{OH}_{OH}$	$^{HO}_{HO}{>}As{-}O{-}As{<}^{OH}_{OH}$	$HO{-}As{=}O$

The salts are formed by precipitation or crystallization from solutions, not by ignition as in the case of the corresponding phosphorus acids

ACIDS	SALTS
Ortho arsenious acid, $As(OH)_3$, or H_3AsO_3	Silver ortho arsenite, Ag_3AsO_3
	Copper hydrogen arsenite, $CuHAsO_3$
Pyro arsenious acid, $As_2O(OH)_4$, or $H_4As_2O_5$	Calcium pyro arsenite, $Ca_2As_2O_5$
	Ammonium pyro arsenite $(NH_4)_4As_2O_5$
Meta arsenious acid, $AsO(OH)$, or $HAsO_2$	Potassium meta-arsenite, $KAsO_2$
	Lead meta arsenite, $Pb(AsO_2)_2$

All the arsenites, except the alkali arsenites, are insoluble in water, and they are decomposed by carbonic and hydrosulphuric acids The soluble arsenites react alkaline owing to hydrolysis. Arsenious acid and its salts are reducing agents, but not so powerful as phosphorous acid and the phosphites Arsenious acid precipitates red cuprous oxide from an alkaline cupric solution When heated, the arsenites are converted into arsenates and free arsenic, and when heated with charcoal, both the arsenates and the arsenites are reduced to arsenic

§ 7 Antimony Trioxide and Antimonious Acid

Antimony trioxide or antimonious oxide is made by burning antimony in air, and by adding hot water to a solution of either antimony trichloride, or antimony sulphate $4SbCl_3 + 6H_2O = Sb_4O_6 + 12HCl$ The precipitated oxide is washed with a solution of sodium carbonate to remove the free acid, and finally with water

[1] With reference to the Styrian arsenic eaters, J F W Johnston (1855) says "Arsenic is consumed chiefly for two purposes—First, to give plumpness to the figure, cleanness and softness to the skin and beauty and freshness to the complexion Secondly, to improve the breathing and give longness of wind, so that steep and continuous heights may be climbed without difficulty and exhaustion of breath Both these results are described as following almost exactly from the prolonged use of arsenic either by men or animals"

Antimonious oxide is a white powder It volatilizes just over 1500°, and its vapour density then corresponds with Sb_4O_6 The vapour condenses in two distinct forms—prismatic needle-like crystals belonging to the rhombic system, and in regular octahedra belonging to the cubic system These crystals are isodimorphous with the corresponding crystals of arsenious oxide The octahedra are deposited nearest to the hot zone, and the prismatic crystals further along in the cooler part A mixture of both will be found in between The two forms occur in nature as the rhombic mineral *senarmontite*, and the cubic mineral *valentinite* The latter crystallizes in well-formed octahedra The former is the variety stable at high temperatures, the latter at low ones

This oxide is very sparingly soluble in water, and the solution has no action on litmus The oxide is insoluble in nitric and sulphuric acids, but it dissolves in hydrochloric acid forming antimony trichloride, $SbCl_3$ The basic qualities of antimony trioxide are also exemplified in its uniting with sulphuric and nitric acids to form salts antimony sulphate, $Sb_2(SO_4)_3$, antimony nitrate, $Sb(NO_3)_3$ The oxide is also readily soluble in an aqueous solution of tartaric acid, $H_2(C_4H_4O_6)$, and in a boiling solution of acid potassium tartrate $HK(C_4H_4O_6)$ The solution furnishes crystals of tartar emetic, or potassium antimonyl tartrate, $2[(SbO)K(C_4H_4O_6)]H_2O$ This is the most important salt of antimony in commerce If hydrochloric acid be added to an aqueous solution of tartar emetic, antimonyl chloride, SbOCl, that is antimony oxychloride, is formed, and if sulphuric or nitric acid be added, ortho-antimonious acid $Sb(OH)_3$, is precipitated because the antimony sulphate or nitrate first formed is immediately hydrolyzed $SbO(NO_3) + 2H_2O \rightleftharpoons HNO_3 + Sb(OH)_3$.

Antimonites and antimonious acids —Ortho antimonious acid is prepared by the action of acids upon tartar emetic as indicated above The corresponding arsenic compound has not been isolated probably because arsenious hydroxide is not so basic as the corresponding antimony compound. Ortho antimonious acid forms a white powder when dried at 100° This hydrate readily loses one molecule of water forming meta-antimonious acid, SbO OH, or $HSbO_2$ Meta-antimonious acid shows its acidic qualities by forming salts—meta-antimonites—when it is dissolved in alkalies, the hydrogen of the acid is replaced by the basic radicle, *e.g* sodium meta-antimonite, $NaSbO_2 \, 3H_2O$, has been obtained in tetragonal crystals It is almost insoluble in water

On boiling antimony trioxide with sodium hydroxide, a solution of sodium ortho-antimonite, $Sb(ONa)_3$ or Na_3SbO_3, is formed The salt is hydrolyzed when the solution is diluted with water $Sb(ONa)_3 + H_2O = 2NaOH + NaSbO_2$, and also into Sb_2O_3 if much water be present The filtered solution deposits crystals of sodium meta-antimonite on cooling The latter is decomposed on further dilution into antimony trioxide Hence, if sodium hydroxide or carbonate be added to antimony trichloride an almost quantitative precipitation of the trioxide, Sb_2O_3, occurs SbO in SbO H, like KO in KO H, behaves as a univalent basic radicle and it is called antimonyl—*e g* antimonyl nitrate, $SbO(NO_3)$, and antimonyl sulphate $(SbO)_2SO_4$ All these compounds are readily hydrolyzed by water and form acid and the trioxide, so that they cannot be made in aqueous solution Pyro-antimonious acid has been reported—$Sb_2O(OH)_4$, or $H_4Sb_2O_5$, but there is some doubt if it has yet been isolated. The

constitution of the antimonites will appear by comparison with the graphic formulæ for the corresponding arsenites.

§ 8 Bismuth Trioxide.

Bismuth trioxide is formed when bismuth is heated in air or when the hydrated oxide, carbonate, or nitrate is calcined. Bismuth trioxide is a cream coloured powder which is not acted on by water. It is the most stable of all the three bismuth oxides. All the three known bismuth oxides form the trioxide when heated in air. Bismuth trioxide melts at 700°. It is dimorphous, and isodi- or rather isotri-morphous with the corresponding oxides of antimony and arsenic.[1] Bismuth trioxide forms three hydrates: $Bi_2O_3.H_2O$, $Bi_2O_3.2H_2O$, and $Bi_2O_3.3H_2O$. These have no acidic properties and do not combine with bases to form salts. The trihydrate is formed by pouring an acid solution of bismuth nitrate into an excess of aqueous ammonia: $2Bi(NO_3)_3 + 6NH_4OH = 6NH_4NO_3 + Bi_2O_3.3H_2O$. This at 100° passes into the monohydrate, $Bi_2O_3.H_2O$. Bismuth trioxide exhibits marked basic properties, for it dissolves in acids to form salts—bismuth nitrate, $Bi(NO_3)_3$, bismuth sulphate, $Bi_2(SO_4)_3$, etc. With a small quantity of hydrochloric acid, it first forms bismuth oxychloride, BiOCl, and with an excess of acid, bismuth trichloride, $BiCl_3$. Water converts all these salts into insoluble basic salts and free acid. The small amount of acid formed is practically without action on the precipitate at the extreme dilution, and precipitation is therefore practically complete: $Bi(NO_3)_3 + 2H_2O = 2HNO_3 + BiO(NO_3).H_2O$.

§ 9 Arsenic Pentoxide, and Arsenic Acids

Arsenic pentoxide cannot be prepared, as in the case of phosphorus pentoxide, by the combustion of arsenic in oxygen gas because the product with arsenic is the trioxide. Arsenic acid, H_3AsO_4, is made by digesting arsenic trioxide with nitric acid. The cold concentrated solution deposits rhombic crystals of $2H_3AsO_4.H_2O$ melting at about 36°; when heated to 100°, the crystals lose their water of crystallization and a crystalline powder once called ortho-arsenic acid, H_3AsO_4, remains. It was also stated that if ortho arsenic acid be heated to about 140° or 180°, pyro-arsenic acid, $H_4As_2O_7$, is formed: $2H_3AsO_4 = H_2O + H_4As_2O_7$, and when this is heated to about 200° it passes into meta-arsenic acid, $HAsO_3$, by the loss of another molecule of water: $H_4As_2O_7 = 2HAsO_3 + H_2O$. As a matter of fact, the existence of only two compounds of arsenic pentoxide with water have been definitely established—*viz.* $As_2O_5.4H_2O$, and $3As_2O_5.5H_2O$. When arsenic acid is heated to 155° for about 14 days, to 170° for about 5 days, or to 210° for 2½ hours, arsenic pentoxide is obtained as a white deliquescent glassy solid: $2H_3AsO_4 = 3H_2O + As_2O_5$. Unlike phosphorus pentoxide, if arsenic pentoxide be heated to a higher temperature—over 440°—it breaks down into the trioxide and oxygen: $2As_2O_5 = As_4O_6 + 2O_2$. Nitrogen pentoxide is also decomposed on heating. Like phosphorus pentoxide, arsenic pentoxide dissolves readily in water forming

[1] A little known bismuth suboxide, BiO, or Bi_2O_2, is said to be formed as a black precipitate when a bismuth salt is reduced by an alkaline solution of stannous chloride. It is possible that the precipitate is a mixture of metallic bismuth and of the hydrated oxide.

tribasic arsenic acid, H_3AsO_4—ortho-arsenic acid. The pyro- and meta-acids are said to resemble the corresponding phosphoric acids, but they are less stable. Metaphosphoric acid is stable at high temperatures, but meta-arsenic acid is decomposed as indicated above. Both the pyro- and meta-arsenic acids form crystalline solids which dissolve in water with the evolution of heat, and the formation of the ortho-acid. Hence, unlike the corresponding phosphoric acids, aqueous solutions of meta- and pyro-arsenic acids cannot exist. Each of the arsenic acids forms salts isomorphous with the corresponding phosphate, but the salts of the meta- and pyro acids, when dissolved in water, pass into the ortho compounds. If the nomenclature indicated when discussing the periodic acids were consistently followed, the ortho-acid would be $As(OH)_5$. The term ortho- is applied to the $AsO(OH)_3$ acid for the same reasons that $PO(OH)_3$ is called orthophosphoric acid.

§ 10 Antimony Pentoxide and Antimonic Acids

Orthoantimonic acid, H_3SbO_4, or $O{=}Sb{\equiv}(OH)_3$. This acid is made by oxidizing antimonious chloride with a concentrated solution of nitric acid, and then diluting the solution with water. A white powder, approximating $Sb_2O_5.6H_2O$, is formed which passes into the ortho-acid, H_3SbO_4, after standing over concentrated sulphuric acid in a desiccator for some time. At 200°, the ortho acid passes into the pyro-acid.

Pyro-antimonic acid, $H_4Sb_2O_7$, can be prepared as just stated, and also by the action of nitric acid on antimony at 100°. The acid obtained by the latter reaction is not constant in composition, for it is probably a mixture of different antimonic acids. The pyro-acid can be most easily made by the action of hot water on antimony pentachloride: $2SbCl_5 + 7H_2O = 10HCl + H_4Sb_2O_7$. The precipitate is dried at 100°. The pyro acid is said to lose water and pass into meta-antimonic acid, $HSbO_3$—sometimes called antimonic acid—pyro antimonic acid, by the way, is sometimes erroneously called "meta-antimonic acid."

Naming the antimonic acids.—There is some confusion in the nomenclature of the antimonic acids. Fashion has been stronger than system. Strictly, the unknown acid, $Sb(OH)_5$, should be called "ortho antimonic acid," but, as in the case of the phosphoric acids, the first dehydration product stable at ordinary temperatures is called "ortho antimonic acid." In conformity with the notation adopted for the phosphoric and arsenic acids, the next dehydration product, $H_4Sb_2O_7$, is called "pyro antimonic acid," and the next dehydration product, $HSbO_3$, "meta antimonic acid." E. Fremy, who first made sodium pyro antimoniate, $Na_2H_2Sb_2O_7.6H_2O$, called it "sodium meta antimoniate," and the corresponding acid, $H_4Sb_2O_7$, "meta antimonic acid," to distinguish it from "antimonic acid." It is best to keep to the uniform system already in use for the arsenic and phosphoric acids.

Antimony pentoxide, Sb_2O_5.—When antimonic acid is heated to between 300°–400°, antimony pentoxide, Sb_2O_5, is formed; this begins to decompose at 440° giving antimony tetroxide, Sb_2O_4, the decomposition is complete at 750° or 800°. Antimony pentoxide is a straw yellow powder, almost insoluble in water. When moistened with water, however, the moist mass reddens blue litmus. Antimony pentoxide dissolves in concentrated hydrochloric acid forming a liquid which has oxidizing properties. For instance, it decomposes potassium iodide with the separation of iodine: $Sb_2O_5 + 4KI + 10HCl = 2SbCl_3 + 4KCl + 2I_2 + 5H_2O$. If the meta-acid be allowed to remain for a long time in contact with water, it forms ortho antimonic acid, H_3SbO_4.

Antimoniates.—All the antimonic acids give antimoniates when treated with an aqueous solution of potassium hydroxide. The normal ortho-antimoniates have not been prepared, but primary salts are known. Numerous salts of pyro- and meta-antimonic acids have been prepared. **Potassium pyro-antimoniate,** $K_4Sb_2O_7$, is best made by adding powdered antimony in small quantities at a time to four times its weight of fused nitre, KNO_3. The fused mass presumably contains **potassium ortho-antimoniate,** K_3SbO_4, but when the cold mass is washed with water, the ortho-salt is decomposed forming potassium pyro-antimoniate, $K_4Sb_2O_7$, and the addition of more water, or by rapid boiling, the salt is gradually changed into the acid salt—**potassium dihydrogen pyro-antimoniate,** $K_2H_2Sb_2O_7.6H_2O$ as granular powder sparingly soluble in cold water, but fairly soluble in hot water. The solution of this salt is used as a test for sodium salts with which it gives a precipitate of **sodium dihydrogen pyro-antimoniate,** $Na_2H_2Sb_2O_7.6H_2O$. On boiling potassium dihydrogen pyro-antimoniate for a long time with an excess of water, it gradually passes into **potassium dihydrogen ortho-antimoniate,** $O{=}Sb(OK)(OH)_2$, which is obtained as a gelatinous precipitate $2KH_2SbO_4.H_2O$ on evaporation of the solution. By further boiling ortho-antimonic acid is formed. All the antimoniates are decomposed by acids giving antimony pentoxide.

Antimony tetroxide, Sb_2O_4.—When antimony trioxide is heated in air it appears to smoulder, forming antimony tetroxide, Sb_2O_4, which is yellow when hot, and white when cold. The powder is almost insoluble in water. The same oxide is formed when antimony pentoxide is heated to a red heat; the dissociation pressure is about 930°. Some consider the tetroxide to be antimonyl metantimoniate, $SbO.SbO_3$; others, antimony ortho-antimoniate, $Sb.SbO_4$. It forms salts—*e.g.* **potassium hypoantimoniate,** $K_2Sb_2O_5$, or $K_2O.Sb_2O_4$—when fused with potash. Hence, antimony tetroxide is generally considered to be the anhydride of an unknown acid **hypoantimonic acid**—$H_2Sb_2O_5$.

§ 11. Bismuth Pentoxide. Bismuthic Acids.

If chlorine be passed into a boiling aqueous solution of potassium hydroxide in which bismuth trioxide is suspended, a dark chocolate brown precipitate is formed: $Bi_2O_3 + KOCl = KCl + Bi_2O_4$. The precipitate is washed with water, dilute nitric acid, and dried at 180°. The precipitate appears to be a mixture of bismuth pentoxide, Bi_2O_5, with bismuth tetroxide, $Bi_2O_4.2H_2O$. The greater the excess and concentration of the lye the greater the yield of tetroxide. The tetroxide is formed when the trioxide is oxidized with potassium ferricyanide in alkaline solutions. In some respects the oxide, Bi_2O_4, resembles antimony tetroxide. When heated above 200°, bismuth tetroxide decomposes into the trioxide Bi_2O_3. If the current of chlorine gas be continued until the precipitate becomes scarlet red, the washed precipitate has approximately the composition $KBiO_3$—**potassium metabismuthate,** corresponding with **metabismuthic acid,** $HBiO_3$. This appears to be rather a feeble acid. The salts are decomposed by water. Potassium bismuthate, $KBiO_3$, is also formed as a dark red deposit on the anode when an almost boiling hot solution of potassium hydroxide (specific gravity 1.13) and potassium chloride in which bismuth trioxide is suspended, is electrolysed in a platinum dish. If the precipitate be

washed and boiled for a short time in dilute nitric acid, scarlet red metabismuthic acid is obtained The ortho-bismuthates are not known When heated between 100° and 120°, bismuthic acid loses its water and some oxygen, and is said to form a little bismuth pentoxide, Bi_2O_5, and the colour changes from red to dark brown. When heated to a higher temperature, bismuth trioxide is formed The dark brown mass suddenly turns deep red at about 300° owing to the formation of a third modification of ordinary bismuth trioxide Bismuth tetroxide is sometimes considered to be a basic salt of bismuthic acid, BiO BiO_3, where BiO is supposed to be a monad radicle The graphic formula usually assigned to the bismuth oxides are

Bismuth trioxide — Bismuth pentoxide — Bismuth tetroxide — Bismuthic acid

Bismuth pentoxide is an unstable brown powder formed as indicated above With hydrochloric, and the oxy-acids, bismuth pentoxide furnishes bismuth salts and chlorine or oxygen thus behaving like antimony pentoxide, and both behave as if they were basic peroxides

§ 12. The Sulphides of Arsenic, Antimony, and Bismuth.

Arsenic trisulphide, As_2S_3 —This sulphide occurs in nature as the mineral *orpiment*—a term derived from the Latin *auri pigmentum*, golden paint Arsenic trisulphide is formed when powdered arsenic and sulphur are heated together in the proportions indicated by the formula, As_2S_3, and it is also precipitated as a canary-yellow solid when hydrogen sulphide is passed into a solution of an arsenious salt acidified with hydrochloric acid (p 620) The same remarks apply, *mutatis mutandis*, to antimony trisulphide, Sb_2S_3, precipitated as a brick-red powder, and to bismuth trisulphide, Bi_2S_3, precipitated as a dark brown powder These sulphides can be fused, and on cooling a brittle crystalline mass is obtained. When heated in air, they are oxidized to the corresponding trioxides

Thioarsenites and thioantimonites —Antimony and arsenic sulphides are soluble in the alkali hydroxides, ammonium carbonate, and alkali sulphides, whereas bismuth sulphide is practically insoluble in these reagents Similar remarks apply to the effect of these reagents upon the oxides of these elements Curiously enough, a compound labelled "insoluble" in a given reagent often dissolves to a certain extent if another soluble compound be present, and some uncertainty is often introduced in analytical processes if this fact be ignored Bismuth sulphide is soluble in concentrated sodium sulphide, but is reprecipitated on dilution Unstable compounds of bismuth sulphide with the alkalies can be obtained by fusing the two substances together With the alkali sulphides, arsenic trisulphide forms compounds called thioarsenites, which may be advantageously regarded as salts of an hypothetical ortho-thioarsenious acid, H_3AsS_3, or $As(SH)_3$ $As_2S_3 + 3(NH_4)_2S = 2As(SNH_4)_3$, and as in the case of the analogous oxy acids, salts of the hypothetical pyro-thioarsenious acid, $H_4As_2S_5$, and meta-thioarsenious acid, $HAsS_2$, have been prepared. The thioarsenites of the alkalies, alkaline earths, and of magnesium are soluble in water, but decompose on boiling The

solutions are also decomposed by acids with the evolution of hydrogen sulphide, and the re precipitation of arsenic trisulphide Hydrogen sulphide will not precipitate arsenic sulphide from the normal arsenites, and it is only partially precipitated from the primary and secondary arsenites, because soluble thioarsenites are formed If sufficient acid be present to prevent the formation of the soluble arsenites, precipitation is complete When arsenic trisulphide is dissolved in an alkaline hydroxide, both arsenite and thioarsenite are formed $2As_2S_3 + 4KOH = 3KAsS_2 + KAsO_2 + 2H_2O$ Similar results apply to antimony sulphide in which case thioantimonites are formed.

Arsenic disulphide, As_2S_2, is found in nature as the mineral *realgar*, and it can be made by heating together sulphur and arsenic in the right proportions, or by heating arsenic sulphide with arsenic, or arsenious oxide and sulphur, or distilling a mixture of iron pyrites and arsenical pyrites Arsenic disulphide is a red brittle vitreous or crystalline solid, it fuses at 307° and sublimes unchanged Heated in air it burns with a blue flame forming sulphur dioxide and arsenic trioxide It is used in pyrotechny, for instance, in the manufacture of the so called "Bengal fire," which is a mixture of realgar, sulphur, and nitre

Arsenic pentasulphide, As_2S_5, can be made by fusing together arsenic trisulphide and sulphur in the right proportions It is precipitated when a rapid stream of hydrogen sulphide is passed through a cold solution of arsenic acid containing a large excess of hydrochloric acid, or through a strongly acidified solution of a soluble arsenate Antimony pentasulphide, Sb_2S_5, is made by the action of hydrogen sulphide on a mixture of antimony pentachloride with a little water Arsenic pentasulphide, As_2S_5, is citron yellow, antimony pentasulphide, Sb_2S_5, is reddish yellow, and bismuth pentasulphide, Bi_2S_5, is black

Thioarsenates and thioantimonates —Like the corresponding trisulphides, arsenic and antimony pentasulphides dissolve in alkali sulphides producing in the one case thioarsenates, and in the other, thioantimonates. With the alkali hydroxides, a mixture of the arsenates or antimonates with thioarsenates or thioantimonates The free thio acid is liberated by acidifying the solution of the thioarsenate or thioantimonate, but the thio acid decomposes at once with the precipitation of the pentasulphide Salts of ortho-thioarsenic acid—say, K_3AsS_4—pyro-thioarsenic acid—$K_4As_2S_7$—and meta-thioarsenic acid—say, $KAsS_4$—have been reported Similar remarks apply to the thioantimonic acids Bismuth pentasulphide does not exhibit the acidic properties shown by the corresponding antimony and arsenic compounds Schlippe's salt, sodium ortho-thioantimonate—$Na_3SbS_4.9H_2O$—is one of the best known thio antimonates. It is formed when antimony trisulphide is boiled with sulphur and sodium hydroxide It crystallizes in colourless tetrahedra The salt is decomposed by acids, depositing antimony pentasulphide The crystals on exposure to air become covered with a yellowish-red crust of antimony pentasulphide owing to the action of the carbon dioxide in the atmosphere

The action of hydrogen sulphide on arsenic acid —The precipitation of pure arsenic pentasulphide from an acidified solution of arsenic acid is almost impossible because some arsenic trisulphide is formed at the same time Concentrated hydrochloric acid in the cold favours the separation of the pentasulphide If hydrogen sulphide be passed into a cold solution of arsenic acid, the separation of the sulphide is very slow—

over twenty-four hours are sometimes needed for the complete precipitation of the arsenic as trisulphide The liquid remains clear for some time, then becomes turbid, and finally arsenic trisulphide is precipitated Solutions containing arsenious acid react with hydrogen sulphide at once, but with solutions containing arsenic acid, it is supposed that three consecutive reactions occur

(1) The slow formation of a thioarsenic acid, H_3AsSO_3, thus $H_2S + H_3AsO_4 = H_2O + H_3AsSO_3$

(2) The reduction of the thioarsenic acid, H_3AsSO_3, to arsenious acid, H_3AsO_3, with the separation of sulphur $H_3AsSO_3 = H_3AsO_3 + S$

(3) The decomposition of the arsenious acid by the hydrogen sulphide $2H_3AsO_3 + 3H_2S = 6H_2O + As_2S_3$

The initial and final stages of the reaction are represented by the equation $2H_3AsO_4 + 5H_2S = 2S + 8H_2O + As_2S_3$ The rate of precipitation of the arsenic trisulphide is determined by the rate of reduction of the arsenic acid to arsenious acid, by the hydrogen sulphide If the solution be heated, the decomposition of the thioarsenic acid is accelerated, but for the rapid precipitation of arsenic trisulphide it is best to reduce the arsenic acid to arsenious acid rapidly by boiling with sulphurous acid before the hydrogen sulphide is used, and not to throw the work of reduction on the slower reducing agent—hydrogen sulphide

§ 13 The Nitrogen Family of Elements

The properties of the group of elements—nitrogen, phosphorus, arsenic, antimony, and bismuth—just considered show a gradual transition from non-metallic nitrogen to metallic bismuth The relationship of the physical properties of the elements is best shown by arranging them in the order of their atomic weights, when the gradual and regular difference between the properties of successive elements is made clear —

TABLE XLIII —PROPERTIES OF THE NITROGEN-PHOSPHORUS FAMILY

	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Atomic weight	14 01	31 0	75 0	120 2	208
Specific gravity	1 026	1 82–2 31	4 69–5 73	6 62	9 78
Atomic volume	13 7	about 15	13 to 16	18	21 3
Melting point	−214°	44°	[480°]	629 2°	270°
Boiling point	−193°	287°	[450°]	1440°	1420°

The changes in the melting and boiling points are not so regular as the other properties, but this may be related to the fact that phosphorus, arsenic, and antimony have four-atom molecules whereas bismuth has probably a two-atom molecule The heat of combination of the different elements with hydrogen shows a somewhat similar gradation NH_3 + 12 Cals, PH_3 + 11 6 Cals, AsH_3 − 36 7 Cals, SbH_3 − 81 8 Cals Ammonia is a relatively strong base, phosphine a feeble base, while arsine and stibine do not show basic qualities The oxy-acids diminish in strength during the passage from nitric to phosphoric, to arsenic to antimonic, to bismuthic acid The acidic properties of the oxides likewise diminish from the strongly acid nitrogen and phosphorus acids, to the feebly acidic oxides of arsenic, antimony, and bismuth The basic property first appears with arsenic and becomes stronger during the passage to antimony and to bismuth. The trichloride of nitrogen is very unstable, while with bismuth

the trichloride is quite stable. The boiling points of the trichlorides increase with increasing atomic weights of the elements, thus NCl_3 boils at 71°, PCl_3, 78°, $AsCl_3$, 130.2°, $SbCl_3$, 200°, and $BiCl_3$, at 447°. The halogen compounds of nitrogen and phosphorus are completely hydrolyzed by water, arsenic trichloride is also hydrolyzed by water, but it can exist in solution in the presence of hydrochloric acid. Antimony and bismuth halides are incompletely hydrolyzed by water. The study of the progressive changes in the properties of these elements could be developed much further, but sufficient has been indicated in what precedes to emphasize the family resemblances.

§ 14 Vanadium, Niobium, and Tantalum

	Vanadium, V	Niobium, Nb	Tantalum, Ta
Atomic weights	51.06	93.5	181

The three elements—vanadium V, niobium Nb, and tantalum, Ta—have many properties which relate them with the nitrogen family. The physical and the chemical properties of the three elements have a family likeness. With the physical properties

TABLE XLIV.—PROPERTIES OF THE VANADIUM FAMILY

	Vanadium	Niobium	Tantalum
Atomic weight	51.06	93.5	181
Colour	Silvery metal	Steel grey metal	Iron grey metal
Specific gravity	5.5	7.06	8
Atomic volume	9.3	13.3	23
Melting point	1730°	1950°	2850°

The relations of these elements with the nitrogen family are often emphasized by the scheme shown in the margin below, where the hyphen represents a supposed element not yet discovered.

History of vanadium.—Del Rio, in 1801, expressed the opinion that a Mexican ore which he analyzed contained a new metal which he called "erythronium"—from the Greek ἐρυθρός (erythros), red—because it furnished red salts when treated with acids. Del Rio abandoned his opinion when Collet-Descostils, four years later, claimed that the supposed new metal was an impure chromium oxide. In 1830, N. G. Sefström described a new mineral which he found in some Swedish iron ores, and suggested for it the name "vanadium"—from "Vanadis," a Scandinavian goddess. Immediately afterwards, F. Wöhler, 1831, established the identity of Sefström's "vanadium" with Del Rio's "erythronium." J. J. Berzelius, 1831, investigated vanadium, and he appears to have been under the impression that the oxide VO was the metal itself. H. E. Roscoe, in 1867, isolated the metal and established its relationship with the nitrogen family of elements.

```
     N
     |
     P
    / \
   V   \
   |    As
   Nb   |
   |    Sb
   Pr   |
   |    —
   Ta   |
        Bi
```

Vanadium.—Vanadium occurs in a few minerals, *e.g.* *vanadinite,*

$Pb_5(VO_4)_3Cl$, etc Small quantities occur in iron ores, and traces occur in most British fireclays and in granitic rocks When the ores are fused with sodium nitrate, sodium vanadate is formed This can be extracted with water When the solution is treated with an ammonium salt, an orange-coloured precipitate of ammonium meta-vanadate, NH_4VO_3, is obtained When this salt is heated, vanadium pentoxide, more or less impure, remains W von Bolton (1908) made coherent rods of vanadium, niobium, and tantalum by moulding small rods of carbon, paraffin, and the pentoxide, and baking them at high temperatures The rods were then heated by passing a moderately strong current through them *in vacuo* This oxide can be fused without decomposition, and it behaves in solution as a weak acid forming a series of salts meta-, pyro-, ortho, tetra-, and hexa-vanadates This element resembles nitrogen in forming several oxides The salts of the different oxides are coloured as indicated below

Salts of	V_2O	V_2O_2 or VO	V_2O_3	V_2O_4 or VO_2	V_2O_5
Colour	—	lavender	green	blue	orange or yellow

The basic properties of vanadium oxides become less and less pronounced as the proportion of oxygen increases The higher oxides exhibit acidic as well as basic properties The element also forms a series of chlorides VCl_2, VCl_3, VCl_4, $VOCl_3$ The existence of VCl_5 is doubtful Unlike nitrogen and phosphorus, vanadium is undoubtedly a metal As in the case of phosphorus, the metal, if heated to a high temperature, burns to the pentoxide, V_2O_5

Vanadium is used in making special steels because very small quantities of vanadium modify the properties of steel by increasing the hardness and malleability of the metal. The addition of a half per cent of vanadium, for instance, raised the tensile strength of a sample of steel from 7½ to 13 tons per square inch The so called ferro-vanadium is a special alloy of iron rich in vanadium made to facilitate the alloying of definite amounts of vanadium with the molten steel

History of niobium and tantalum —In 1801, C Hatchett analyzed some chromium minerals from Connecticut, and found an earth hitherto unknown. He named the mineral "columbite," after the place of its origin, and the element was designated "columbium." A year later, 1802, A. G Ekeberg found a new element in some Finnish minerals resembling columbite To this he gave the name "tantalum" from "Tantalus" of Grecian mythology, in allusion to the "tantalizing" difficulties he encountered in dissolving the mineral in acids In 1844, H. Rose noticed two new elements in a sample of columbite from Bodenmais one, tantalum, is similar to Ekeberg's tantalum, and the other has been called "niobium," from Niobe the mythological daughter of Tantalus Hatchett's "columbium" was probably a mixture of both tantalum and niobium The term "columbium" was once applied to Rose's niobium

Niobium, Nb, and tantalum, Ta —These two elements are found associated in the isomorphous minerals *tantalite*, $Fe(TaO_3)_2$, and columbite or *niobite*, $Fe(NbO_3)_2$ One or both of the elements occur in several rare earths—monazite, and yttrotantalite—and also in tinstone, pitchblende, wolfram, and many other minerals Niobium forms a mono, di-, and a penta-oxide, and tantalum a di- and a penta-oxide Niobium forms both a tri- and penta-chloride, while tantalum forms the penta-chloride Both elements exhibit feeble base-forming qualities, and their chief

compounds are the niobates and the tantalates The elements are produced when the chlorides are reduced in a current of hydrogen Tantalum forms a series of complex salts with alkaline fluorides Thus, K_2TaF_7 is formed in rhombic needles when a solution of tantalic acid in hydrofluoric acid is treated with potassium fluoride The sparing solubility of this salt in hydrofluoric acid enables tantalum to be separated from niobium. Niobium metal melts at about 1950°, tantalum about 2300° The metal tantalum is used as a filament in incandescent electric lamps—"tantalum lamps."

Didymium or rather praseodymium (Pr) and neodymium (Nd) members of the rare earth series (*q v*), probably belong to this family, and lie between niobium and tantalum. Comparatively little is known about these elements.

Questions

1 State what would be observed and the nature of the changes which occur, in each of the following cases (equations not required) (*a*) when phosphorus trichloride is added to a considerable volume of water, (*b*) when bismuth trichloride is added to a considerable volume of water, (*c*) when a hot acid solution of potassium permanganate is treated with hydrogen sulphide, (*d*) when an alkaline chromate solution (as $KCrO_2$, a salt derived from Cr_2O_3) is treated with sodium peroxide and converted into a salt derived from CrO_3—*Massachusetts Inst Technology, U S A*

2 Compare the hydrides of nitrogen, phosphorus, arsenic, antimony—*Univ Pennsylvania U S A*

3 Describe carefully the preparation of gaseous hydride of phosphorus and compare its properties with those of the corresponding hydrides of nitrogen and arsenic.—*Sheffield Univ*

4 What are the chief sources of white arsenic? How can this substance be converted into (*a*) arsenic acid, (*b*) Scheele's green (*c*) arsenuretted hydrogen? By what property can arsenuretted hydrogen be distinguished from ammonia and from phosphine?—*London Univ*

5 Arsenious acid is less soluble in normal hydrochloric acid than in pure water, and increase in the concentration of the acid leads to a further diminution in the solubility of the oxide until, when the concentration of the acid reaches 3 2 normal, the solubility of the arsenious acid becomes a minimum, the solubility afterwards rising as the concentration of the acid is still further increased Discuss and explain these results—*St Andrews Univ*

6 Discuss the following changes and suggest an explanation applicable to both of them—(*a*) when concentrated hydrochloric acid is mixed with concentrated brine a precipitate is formed which disappears on the addition of water, (*b*) when water is mixed with bismuth chloride solution a precipitate is formed, which disappears on the addition of concentrated hydrochloric acid—*London Univ*

7 Which of the elements are to be regarded as most similar to nitrogen? Indicate the grounds on which your answer is based—*Aberdeen Univ*

8 Why are phosphoric and arsenic acids regarded as "tribasic acids" when they yield salts such as those of the formula Na_2HPO_4, and Na_2HAsO_4 on neutralization with sodium carbonate? Formulate meta, ortho, and pyrophosphoric acids in accordance with (*a*) the old dualistic theory of the composition of acids and salts, and (*b*) the modern theory What facts apparently justify the latter?—*London Univ*

9 In what forms does arsenious oxide exist? What happens when the oxide is (*a*) introduced into an apparatus in which hydrogen is being generated, (*b*) heated, (*c*) heated with charcoal, (*d*) heated with dilute nitric acid?—*London Univ*

10 Describe the action of water (*a*) in small and (*b*) in large quantity on the chlorides of phosphorus, arsenic, and antimony—*Board of Educ*

11 How is arsenic obtained and how would you prepare arsenic chloride, arsenic trioxide and arsenic acid from arsenic? What are the more characteristic properties of these substances?—*Board of Educ*

CHAPTER XXXIII

BORON, ALUMINIUM, AND RELATED ELEMENTS

§ 1 Boric Acids and the Borates

Extraction—Volcanic jets of steam (soffioni) at a temperature between 90° and 120°, issuing from the fumaroles on the so called Maremme di Toscana—or Tuscany Marshes—carry small quantities of boric acid The steam condenses in lagoons (lagoni) of water which often surround the jets The water of the lagoons becomes highly charged with the acid, and the boric acid can be obtained in a crystalline condition by evaporating the water of the lagoons Artifical lagoons for arresting the jets of steam were established in Tuscany in 1818, and artificial soffioni were bored in 1854. The natural heat of the steam is utilized in concentrating the water The crude acid—called Tuscany acid—is contaminated with ammoniacal salts, etc, and it is coloured yellowish brown The crude acid contains about 82 5 per cent of boric acid, and it can be refined by dissolving it in hot water, and mixing the solution with freshly ignited powdered charcoal This removes the colouring matters The clear solution is then allowed to crystallize, and this is placed on the market as "refined boric acid" or "refined boracic acid." The water of the hot springs at Sulphur Bank and other places in Nevada and California is rich in borates

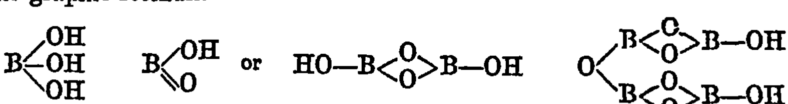
Action of solvents—Boric acid crystallizes during the cooling of its hot aqueous solutions as white shining plates belonging to the triclinic system When the aqueous solution is boiled, the acid volatilizes with the steam, 100 grams of water at 100° dissolve 27 5 grams of H_3BO_3, at 50°, 8 8 grams, and at 0°, 1 95 grams Boric acid is more soluble in alcohol than in water The alcholic solution burns with a characteristic flame tinged with green, and in this way, 0 001 gram of boric acid can be detected in a solution containing 0 1 per cent of the acid. The aqueous solution turns blue litmus claret-red, and moist yellow turmeric paper is coloured brown. Unlike the brown colour produced by alkalies with tumeric paper, the boric acid stain is not destroyed by acids In a solution acidified with hydrochloric acid, 0 0001 gram of boric acid in a solution containing 0 01 per cent, will give a pink coloration when the paper is dried at 100°, if too much acid be present, the stain will be brown, and if no acid be present, the colour does not show

Titration of boric acid—As is the case with carbonic acid, boric acid is not affected by methyl orange If phenolphthalein be used as indicator, and the boric acid be titrated with sodium hydroxide, the pink colour of the phenolphthalein appears before all the boric acid is neutralized This

is due to the hydrolysis of the alkaline borate. If mannite or glycerol (free from acid) is added to the solution, the hydrolysis is prevented, hence the end point of the titration is reached when the red colour of the phenolphthalein persists when more mannite is added. The reaction which occurs during the titration is $NaOH + H_3BO_3 = NaBO_2 + 2H_2O$.

Action of heat.—Boric acid is a tribasic acid, and it has the ultimate composition H_3BO_3, or $B(HO)_3$. A solution containing 22.38 per cent raised the boiling point of water 1.90°, hence, from the formula on p. 215, $5.2 \times 22.38 \div 1.90 = 62.7$. The theoretical number for H_3BO_3 is 62. Hence with boron tervalent, this acid is **orthoboric acid**, $B(OH)_3$. If heated to 100°, orthoboric acid loses water and forms **metaboric acid**, HBO_2, also written $H_2B_2O_4$. 1.1 gram of metaboric acid dissolved in water lowered the freezing point 0.490°. Hence from the formula on p. 218, $18.5 \times 1.1 \div 0.49 = 42.8$, corresponding with the formula HBO_2. If heated to 140°, boric acid forms **tetraboric acid**, or the so-called "pyroboric acid," $H_2B_4O_7$: $4H_3BO_3 = 5H_2O + H_2B_4O_7$. When boric acid is heated to a still higher temperature—"red heat"—it forms anhydrous boron trioxide, or boric oxide. The fused mass solidifies to a colourless transparent glass which absorbs moisture from the atmosphere, and becomes opaque, finally passing into boric acid. (Anhydrous silica does not combine directly with water.) Boric oxide volatilizes extremely slowly at a red heat. Sulphuric acid, it will be remembered, is not so strong an acid as hydrochloric acid at ordinary temperatures, but, owing to the more volatile nature of hydrochloric acid, the less volatile and weaker sulphuric acid is able to convert the chlorides into sulphates, as indicated previously. Similarly, in consequence of the non-volatility of boric acid at a red heat, it is able to decompose the compounds of the stronger acids with the bases and form borates: $B_2O_3 + 3K_2SO_4 = 2B(OK)_3 + 3SO_3$. Sulphuric and hydrochloric acids are much stronger than boric acid when competing for the bases in aqueous solutions, but at a red heat, the more volatile acids are driven off.

Constitution.—The three boric acids are related by the empirical formulæ: orthoboric acid, $B_2O_3.3H_2O$; metaboric acid, $B_2O_3.H_2O$; and tetraboric acid, $2B_2O_3.H_2O$. The relationship is perhaps best shown by the graphic formulæ:



Orthoboric acid, $B(OH)_3$. Metaboric acid, $BO(OH)$ or $H_2B_2O_4$. Tetraboric acid, $H_2B_4O_7$.

The meta- and pyro-boric acids immediately pass to orthoboric acid in aqueous solution.

Orthoborates.—The salts of orthoboric acid are unstable and few well-defined orthoborates are known. Magnesium orthoborate, $Mg_3(BO_3)_2$, is one of the best known orthoborates. There is no doubt about the tribasicity of the acid, however, because the hydrogen of $B(OH)_3$ has been successively replaced by organic radicles such as C_2H_5. Thus, ethyl orthoborate has a vapour density corresponding with $B(OC_2H_5)_3$. This latter compound is formed as a volatile compound in the flame test for boric acid.

Metaborates —The metaborates appear to be the most stable salts of boric acid Potassium forms a metaborate, KBO_2, and a series of potassium acid borates—KBO_2 HBO_2, or KHB_2O_4, and the KBO_2 $3HBO_2$

Tetraborates or pyroborates —These are also stable compounds The best known is borax, $Na_2B_4O_7$ $10H_2O$ A series of complex calcium and magnesium borates occur in nature borocalcite, CaB_4O_7 $6H_2O$, from Iquique, boronatrocalcite (ulexite), $Na_2B_4O_7$ $2CaB_4O_7$ $18H_2O$, from Chili, boracite, $2Mg_3B_8O_{15}$ $MgCl_2$, from the Stassfurt deposits, pandermite, $Ca_2B_6O_{11}$ $4H_2O$, from Panderma in Asia Minor, colemanite, etc

The borates nearly always contain water of crystallization, and, excepting the alkaline borates, they are but slightly soluble in water The borates are easily decomposed by water, and acidulated solutions of the borates give the flame and other reactions characteristic of boric acid In some places boric acid is made directly from the native calcium borates by dissolving the mineral in hot hydrochloric acid and collecting the crystals of boric acid which separate on cooling The acid can also be made by the action of sulphuric or hydrochloric acid on borax

Boric oxide, like alumina, is an "intermediate oxide," for it has feeble acidic and feeble basic properties As a weak acid it forms a series of salts—borates Boric oxide also forms complex salts—boro-silicates—with the metallic oxides and silica, *e g* tourmaline Boric oxide probably plays the same *rôle* in the boro silicates as it plays in the boro tungstates, and alumina in the alumino silicates Corresponding with the basic properties of the oxide, unstable compounds like the acid sulphate, $B(HSO_4)_3$, phosphate, BPO_4, etc, have been formed Most of the salts are hydrolyzed by water, dilute acids, and dilute alkaline solutions

Perborates —When a mixed solution of borax and sodium hydroxide is electrolyzed, or treated with hydrogen peroxide, sodium perborate $NaBO_3$ $4H_2O$ is formed—possibly $NaO-O-B=O$ The perborates act as strong oxidizing agents

§ 2 Borax

Manufacture —Borax occurs as a natural deposit—*tincal*—in the dried-up inland lakes in some parts of India, Tibet, and California—*e g* the "borax marsh" in the Saline Valley Native tincal contains about 55 per cent of borax proper $Na_2B_4O_7$ $10H_2O$ This is extracted by lixiviating the mass with water, and evaporating the clear solution until the crystals separate Before 1870, most of the borax used in Europe was made by digesting a solution of boric acid with the proper amount of soda ash, whereas the borax now in commerce is usually made from native calcium borates The powdered mineral is boiled with a slight excess of an aqueous solution of sodium carbonate Calcium carbonate is precipitated as a "mud" $Ca_2B_6O_{11} + 2Na_2CO_3 \rightleftharpoons 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$ On crystallizing the clear solution, crystals of borax are obtained Carbon dioxide is blown through the mother liquid to convert the sodium metaborate into borax $4NaBO_2 + CO_2 \rightleftharpoons Na_2CO_3 + Na_2B_4O_7$ The borax separates in fine crystals, leaving sodium carbonate in the solution The residual "mud" is compressed in a filter press to remove the soluble matters it contains

The action of water.—100 grams of water at 10° dissolve 1 6 grams

of borax, $Na_2B_4O_7$, at 50°, 10 5 grams, and at 100°, 52 5 grams. The aqueous solution has a feebly alkaline reaction owing to hydrolysis In concentrated aqueous solutions $Na_2B_4O_7 + 3H_2O \rightleftharpoons 2NaBO_2 + 2H_3BO_3$, and on further dilution, hydrolysis may be practically completed $NaBO_2 + 2H_2O \rightleftharpoons NaOH + H_3BO_3$ If a saturated solution be allowed to crystallize above about 62°, octahedral crystals of the pentahydrate, $Na_2B_4O_7\ 5H_2O$, separate, and if the temperature be below this transition point ordinary monoclinic crystals of the decahydrate, $Na_2B_4O_7\ 10H_2O$, are obtained

Titration of borax—A dilute solution of borax may be titrated with standard hydrochloric acid until all the soda is neutralized and the boric acid is all free, provided methyl orange be used as indicator The reaction is $Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3$ The boric acid has no effect on the methyl orange If the same amount of the standard acid be added to the same amount of the borax solution, and phenolphthalein be used as indicator, the freed boric acid can be titrated as indicated previously In this manner, the amount of alkali, and the amount of boric acid in a sample of borax can be determined

The action of heat—When heated, borax fuses, loses water, and swells up into a white porous mass, owing to the expulsion of the water Finally the borax melts to a clear glass—borax glass—which is anhydrous borax Like boric acid, fused borax dissolves many colouring oxides, giving glasses with a characteristic colour The borax "beads" used in flame testing are based on this fact Thus

TABLE XLV—COLOURS OF BORAX BEADS WITH SOME METALLIC OXIDES

Metallic oxide	Oxidizing flame	Reducing flame
Copper	Green (hot), blue (cold)	Colourless or red
Cobalt	Blue	Blue
Chromium	Green	Green
Iron	Yellow (cold); brown (hot)	Dirty green or olive.
Nickel	Violet (hot), yellowish brown (cold)	Grey and opaque
Manganese	Amethyst	Grey and opaque

The dissolution of metallic oxides in fused borax is supposed to be connected with the fact that borax contains an excess of acid anhydride. $2NaBO_2\ B_2O_3$ The union of the metallic oxide with the B_2O_3 forms a metaborate Thus, with copper, $Na_2B_4O_7 + CuO = Cu(BO_2)_2 + 2NaBO_2$

Uses—Large quantities of borax are used in the manufacture of enamels, glazes, and of optical glass, in preserving articles of food if its use is not restricted by law, as a mild antiseptic for making lotions and ointments, in the manufacture of soap, as a cleansing and stiffening agent in laundry work, for stiffening candle wicks, in making varnishes for metals, manufacture of drying oils, with casein as a substitute for gum arabic, as a flux, and in soldering and brazing Solder only adheres to clean metal surfaces, and molten borax will often dissolve the contaminating oxides which prevent solder adhering

§ 3. Boron.

Isolation of the element.—The element boron is made by heating the oxide with sodium, or with potassium, magnesium, or aluminium in a covered crucible $B_2O_3 + 6K = 3K_2O + 2B$ The fused mass is boiled with dilute hydrochloric acid, and a dark brown powder of amorphous boron remains By using magnesium powder, H Moissan (1892) made a sample of amorphous boron containing 99 6 per cent of the element, and but 0 4 per cent of impurity Crystalline boron can also be made as well as the amorphous powder By dissolving boron in molten aluminium at a high temperature, the solution on cooling deposits crystals of boron The aluminium can be removed by boiling the mass with a solution of sodium hydroxide The insoluble boron remains behind in transparent yellow, or yellowish-brown (monoclinic) crystals Crystalline boron is always contaminated with a little aluminium and carbon Some think that the alleged crystalline boron is really a compound of aluminium and boron—AlB_{12}, or $B_{48}C_2Al_3$, for example

Properties.—Amorphous boron does not melt in the electric arc, but it volatilizes a little at that temperature It is oxidized by carbon monoxide and by silica It is attacked by the oxy-acids, and by steam It is said to be slightly soluble in water, giving the solution a brown colour from which it is precipitated by acids and salts These facts make it probable that the solution is colloidal (p 254) Crystalline boron is not attacked by concentrated nitric acid, and aqua regia attacks it but slowly Boiling sodium hydroxide has no appreciable action, but fused sodium hydroxide dissolves it slowly, forming sodium borate and hydrogen

Compounds with other elements.—Boron burns to the trioxide when heated to about 700° in air, and when heated in nitrogen or ammonia it forms boron nitride, BN This compound is decomposed by steam $BN + 3H_2O = B(OH)_3 + NH_3$ The occurrence of ammonia and boric acid in the vapours of the soffioni of Tuscany has led to the theory that these compounds are derived from the action of steam on subterranean boron nitride Boron combines with carbon and silicon at the temperature of the electric arc furnace Carbon boride, CB_6, and silicon borides, SiB_3, and SiB_6, are very hard crystalline substances, which in many ways resemble the diamond and crystalline boron and silicon They resist attack by most chemical agents Metallic borides are formed by the direct union of the elements—Pt, Ag, etc —at a high temperature Thus, magnesium boride, Mg_3B_2, more or less impure, is made by strongly heating a mixture of boron trioxide with magnesium powder $6Mg + B_2O_3 = 3MgO + Mg_3B_2$ Calcium boride in contact with water gives hydrogen and hydrogen boride, and thus behaves unlike calcium carbide which gives acetylene Boron also combines with sulphur, forming boron sulphide, B_2S_3 This compound is best made by passing the vapour of carbon disulphide over a mixture of carbon and boron trioxide at a red heat $2B_2O_3 + 3C + 3CS_2 = 6CO + 2B_2S_3$ Boron sulphide is a yellow crystalline solid with an unpleasant smell The vapour attacks the eyes In contact with water, the sulphide is immediately hydrolyzed, forming boric acid and hydrogen sulphide $B_2S_3 + 6H_2O = 2B(OH)_3 + 3H_2S$ For compounds with the halogens, see below

Occurrence.—The element does not occur free in nature, but it occurs

as boric acid, also called Tuscany boric acid, tincal, boracite, and the complex calcium borates, already discussed, are the chief modes in which boron occurs in nature Boric oxide has been reported in sea water—0 2 gram per cubic metre It is also found in small quantities in soils, plant ashes, in some wines, etc

Atomic weight —The combining weight of boron has been determined from the weight of water present in a given weight of crystalline borax, $Na_2B_4O_7.10H_2O$, and by the analysis of boron carbide, chloride, bromide, and sulphide, etc The results show that if oxygen be taken 16, boron has a combining weight ranging between 10 82 and 11 05, the best representative value is supposed to be 11 Dulong and Petit's rule cannot be used because of the "abnormal" specific heat of this element, Fig 212 Several volatile compounds of boron are known, and the vapour densities of a number of these compounds lead to the inference that the number 11 also represents the atomic weight

History —Although mentioned in the early Latin writings on chemistry, it is probable that the term "borax" did not then refer to the substance now called "borax." In 1702, W Homberg made boric acid from borax, and called it *sal sedativum* Baron, 1748, showed that borax is a compound of Homberg's sal sedativum and soda After Lavoisier's work on acids, the term boracic acid was substituted for sal sedativum, and "boracic acid" was later abbreviated to "boric acid" J L Gay Lussac and J Thenard isolated the element in a more or less impure condition in 1808

§ 4 Boron Hydrides, and Halides

Boron hydrides —When magnesium boride is slowly added to dilute hydrochloric acid at about 50° while a stream of hydrogen passes through the apparatus, the gases which are evolved, when cooled by liquid air, furnish a white crystalline solid with the empirical formula BH According to A Stock (1913–15), this solid is a mixture of various boron hydrides, with silicon hydride, carbon dioxide, and other impurities By fractional distillation of the product, tetraboron hydride, B_4H_{10}, boiling at 16°–17° under ordinary pressure, and a hexaboron hydride, B_6H_{12}, boiling at about 100° were obtained The former decomposes at 100°, forming diboron hexahydride, a gas boiling between −87° and −88° If the diboron hydride is heated at 115°–120° for some time it forms decaboron hydride, $B_{10}H_{14}$, a white solid melting at 99 5° Three other hydrides have been obtained, but nothing corresponding with the *triborene*, B_3H_3, or with the BH_3 or B_3H were noticed

Boron trihalides —All four halogens unite with boron to form trihalides

	BF_3	BCl_3	BBr_3	BI_3
Condition	Colourless gas	Colourless liquid	Colourless liquid	White solid
Specific gravity		1 35 (17°)	2 69	3 3 (50°)
Boiling point	−101° (melts −127°)	18 2°	90 5°	210° (melts 43°)

The first three compounds can be made by the direct union of the elements,

and all four can be made by heating an intimate mixture of boron trioxide and charcoal in a current of the respective gas $B_2O_3 + 3C + 3Cl_2 = 3CO + 2BCl_3$. Boron chloride and fluoride can also be made by the respective action of hydrochloric or hydrofluoric acid upon boron, or on boric oxide, say, by heating a mixture of concentrated sulphuric acid calcium fluoride, and boric oxide $B_2O_3 + 6HF = 2BF_3 + 3H_2O$ A similar process with silica furnished silicon tetrafluoride, SiF_4, but not silicon tetrachloride, $SiCl_4$ This is probably due to the fact that boron trichloride is not quite so readily hydrolyzed as silicon tetrachloride by the water formed in the reaction However, all the boron trihalides are hydrolyzed by water $BF_3 + 3H_2O = B(OH)_3 + 3HF$. The hydrogen fluoride, so produced, unites with some of the unchanged boron trifluoride, BF_3, producing a complex monobasic acid—hydrofluoboric acid, HBF_4, thus $BF_3 + HF = HBF_4$ A series of corresponding salts called borofluorides or fluoborates have been obtained Corresponding chloro- and bromo-borates have been reported Boron fluoride unites with ammonia forming a series of compounds $BF_3 NH_3$, $BF_3 2NH_3$, $BF_3 3NH_3$, similar compounds are obtained by the union of BF_3 with PH_3 An excess of water is needed for the complete hydrolysis of the trichloride If but a small quantity of water be used, a solid hydrate is produced.

§ 5 Aluminium—Occurrence, Preparation, and Properties.

Occurrence—Aluminium, once also called aluminum, does not occur free in nature, but its compounds are numerous and widely distributed. It comes third, after oxygen and silicon, on Clarke's list *Corundum, ruby,* and *sapphire* are more or less impure forms of the oxide, Al_2O_3, *emery* is a mixture of iron oxide and corundum There are three recognized hydrates occurring in nature—*gibbsite* or *hydrargillite,* $Al_2O_3 3H_2O$, or $Al(OH)_3$, *bauxite,* $Al_2O_3 2H_2O$, or $Al_2O(OH)_4$, and *diaspore,* $Al_2O_3 H_2O$, or $AlO(OH)$ The word bauxite is used in rather a general way for native aluminium hydroxides containing the equivalent of, say, 50 to 70 per cent of Al_2O_3, about 25 to 30 per cent of water, with more or less ferric oxide, titanic oxide, and silica Some bauxites approximate to the trihydrate, others appear to be mixtures of the trihydrate and lower hydrates The bauxites are often classed as ferruginous, and non-ferruginous The double fluoride—*cryolite,* $AlF_3 3NaF$, is discussed on p 278, *turquoise* is a hydrated phosphate The *felspars* and *clays,* as well as a great number of common minerals, are complex silicates of aluminium with other bases Bauxite and cryolite are the chief compounds used in the preparation of the metal aluminium

History—The word "alumen," or its Greek equivalent, was formerly applied as a grouping term for substances with an astringent taste Geber and some others classed alum with the "vitriols," but Paracelsus considered it to be radically different, for he pointed out that its "corpus" is not metallic but an intimate mixture of earths The earthy "corpus" was confused with lime until J H Pott, 1746, showed that the base is really an argillaceous earth, and in 1754, A S Marggraf proved clearly that the base is entirely different from lime, and that clay contains the "alum" earth united with silica.

Isolation of the metal.—After Davy's work on potassium, calcium, etc., many attempts were made to isolate the unknown element in alumina and F. Wöhler succeeded in reducing anhydrous aluminium chloride, $AlCl_3$, to the metal by warming the chloride with potassium: $AlCl_3 + 3K = 3KCl + Al$. Wöhler's first experiments furnished a light grey metallic powder, and it was not until 1845 that the compact metal was obtained. The metal was at that time a "chemical curiosity." In 1855, aluminium sold at the rate of about £120 per kilogram, and in 1910, about £80 per ton. H. St. C. Deville, in 1854, reduced aluminium chloride in quantity by means of sodium in place of Wöhler's potassium; H. Rose, 1855, recommended the reduction of cryolite by sodium; and N. Beketoff, the reduction of cryolite by magnesium. These chemical processes are not now used on an industrial scale.

R. Bunsen isolated aluminium by the electrolysis of the fused chloride in 1854, and the result was confirmed by Deville in the same year. A. and E. H. Cowles Bros., 1884, reduced alumina by heating it with carbon in an electric arc furnace. The formation of aluminium carbide, Al_4C_3, introduced some practical difficulties. The method was for a time more or less successfully employed in making alloys of aluminium with copper. The electric furnace was charged with corundum, carbon, and metallic copper. After the charge had been heated about five hours, a copper-aluminium alloy was obtained. The cheap production of aluminium was made possible by the discovery, by C. M. Hall, in 1886, that a solution of alumina in a molten mixture of cryolite and some other fusible fluoride, say potassium fluoride, is an electrolyte, and, when electrolyzed, aluminium collects at the cathode, oxygen at the anode. Patents by C. S. Bradley (1883–1891), P. L. T. Héroult (1887 *et seq.*), and many others embodied ideas more or less valuable, and, as a result, aluminium can now be made cheaply on a large scale. Electrolytic processes are practically the only methods used for the preparation of aluminium.

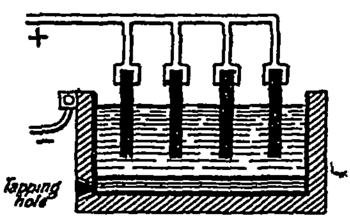


FIG. 224.—Héroult's Aluminium Furnace (Diagrammatic).

Héroult's electrolytic process for aluminium.—In this process the electrolyte is a solution of bauxite in fused cryolite. The "electrolytic cell" is a rectangular iron box (about 8 feet long and 6 feet wide). This cell—Fig. 224—is connected with the electric generator so that the iron box itself serves as the cathode. The anode, or rather anodes, is a set of about 48 carbon rods (3 inches diameter and 15 inches long) arranged in three or four rows and suspended from copper rods connected with the other pole of the generator. The resistance of the electrolyte to the current gives enough heat to keep the mass fluid. The liquid metal sinks to the bottom of the cell, whence it is "tapped" from time to time. The oxygen evolved at the cathode either escapes as a gas or unites with the carbon to form carbon monoxide which either burns or escapes. The process is continuous for fresh supplies of bauxite are added when needed. The resistance of the bath increases when the alumina wants replenishing; and this causes a lamp shunted off the main circuit, to glow. This tells the workmen that a fresh charge of bauxite is needed.

Although clays usually contain the equivalent of 20 to 36 per cent of alumina, no method is known for separating silica from the alumina cheaply enough for use on a manufacturing scale It is necessary to use a fairly pure bauxite for the process, otherwise the metallic aluminium will be seriously contaminated with impurities. Apart from the cost of the electrical energy, the purification of the raw bauxite is the most costly item in the process Native bauxite is usually too impure to be used without a preliminary purification to remove the iron, titanium, and silicon oxides.

Purification of bauxite —The bauxite may be fused with sodium hydroxide or sodium carbonate $Al_2O_3 + 3Na_2CO_3 \rightarrow 2Al(ONa)_3 + 3CO_2$, and the cold mass extracted with water, or better, the bauxite may be roasted at a low temperature to convert the ferrous oxide into ferric oxide, and then digested with a solution of sodium hydroxide in iron kettles under pressure $Al(OH)_3 + 3NaOH = Al(ONa)_3 + 3H_2O$ The alumina is precipitated from the solution by C J Baeyer's process, 1887, namely by agitation with a little aluminium hydroxide, when the aluminium hydroxide separates from the solution until the ratio $Al_2O_3 : Na_2O$ is about 1 : 6 The aluminium hydroxide can also be precipitated by passing carbon dioxide through the solution $2Al(ONa)_3 + 3CO_2 + 3H_2O = 2Al(OH)_3 + 3Na_2CO_3$ The aluminium hydroxide in either case is washed, dried, and ignited.

Properties —Aluminium is a bluish white metal capable of taking a high polish The dull surface usually seen on the metal is an effect of a superficial film of oxide Aluminium is lighter than most metals, its specific gravity is 2 6, and therefore it has nearly the same specific gravity as glass, and one-third the specific gravity of iron The metal is ductile and malleable at 100° to 150° With frequent annealing it can be rolled into sheets, wire, and foil. Aluminium is not very tenacious, at 530° it is so friable that it can be pulverized It is a good conductor of heat and electricity Aluminium melts at about 657°, and boils at 1800°

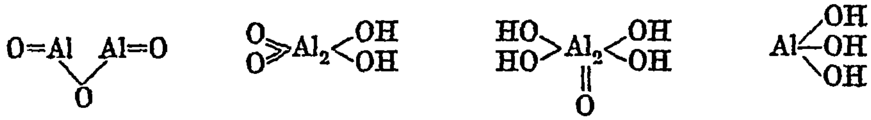
Aluminium remains practically unaltered in dry air, while in moist air and in boiling water, a superficial film of oxide seems to protect the metal from further action Even at 700° to 800° it oxidizes but slowly, at higher temperatures it burns brilliantly with the evolution of much heat In virtue of its intense electropositive character, aluminium is a powerful reducing agent Aluminium powder when intimately mixed with many metallic sulphides or oxides—manganese, chromium, tungsten, uranium, iron, etc.—along with some flux, say, fluorspar, when ignited, reduces the oxides or sulphides to the metal *E g* with pyrites, it forms aluminium sulphide and metallic iron The mixture becomes very hot during the reaction and a temperature of 3000°–3500° is sometimes attained The heat of this reaction can be utilized for softening and welding iron rails, steel castings, etc, where an intense local heat is needed The rails to be welded are packed in a mixture of iron oxide and aluminium powder together with a special cement to make the mass compact When the mass is ignited, it burns and heats the rails to a temperature high enough to weld the metals together The mixture of aluminium powder with various metallic oxides is sold as "thermite," and the process is called H. Goldschmidt's or the aluminothermic process

Aluminium, when heated with the halogens and with nitrogen, forms

because aluminium wire though thicker than copper for a given conductivity is not so heavy and does not strain the supports so much Aluminium is used as a reducing agent in the production of certain metals—chromium, etc —and in the manufacture of "thermite" The formation of oxides during the melting of many metals is prevented if a little aluminium be present, hence aluminium—0 16 to 0 05 per cent —is commonly added to molten steel as it comes from the Siemens-Martin's, or Bessemer's furnace This enables castings to be made more free from "blow holes" Aluminium is difficult to solder, and therefore the parts of large articles are commonly welded together by autogenous soldering

§ 6 Aluminium Oxide and Hydroxide

Three hydroxides of aluminium occur in nature, and they can be represented graphically, though empirically, by assuming that aluminium is a triad, and that alumina, or corundum, is approximately Al_2O_3, or,



Corundum—Al_2O_3 Diaspore—$Al_2O_2(OH)_2$ Bauxite—$Al_2O(OH)_4$ Gibbsite—$Al(OH)_3$

The gelatinous precipitate which is obtained when ammonia or an alkaline carbonate is added to a solution of an aluminium salt, is a colloidal aluminium hydroxide—$Al(OH)_3$—and it contains more or less absorbed water, $AlCl_3 + 3NH_4OH = Al(OH)_3 + 3NH_4Cl$ The curve obtained by measuring the rate at which the gelatinous hydrates lose water on a rising temperature does not show, in a convincing manner, the transition from one hydrate to the other Aluminium hydroxide can be obtained in the sol (hydrosol) condition by dialyzing an aqueous solution of aluminium chloride, or a solution of freshly precipitated aluminium hydroxide in aluminium chloride or aluminium acetate, and in the gel (hydrogel) condition by adding some coagulating salt as indicated on p 387 Freshly precipitated aluminium hydroxide dissolves easily in acids and in alkaline hydroxides If the precipitate has stood a long time under water, or if the precipitate be dried, it dissolves very slowly in these reagents

When aluminium hydroxide is precipitated in a solution containing a colouring matter, the latter is simultaneously precipitated, and the aluminium hydroxide with the absorbed colouring matter is called a lake Advantage is taken of this property in dyeing cloth The aluminium hydroxide is first precipitated in the fibres of the cloth, and the fabric is then immersed in the dye, and some of the dye is fixed by the aluminium hydroxide in the fibres Hence, aluminium hydroxide is a dye fixing agent or mordant Dyes which stain the fibres directly need no mordant

Aluminium hydroxide as a basic oxide—Aluminium hydroxide is amphoteric, for it exhibits both feebly acidic and feebly basic properties The existence of salts like aluminium chloride, aluminium sulphate, etc, is evidence of the basic qualities, and the feeble basic qualities of the

hydroxide is indicated by the fact that salts with the weak acids—carbonic, hydrosulphuric, and sulphurous *acids—do not exist in aqueous* solution

Aluminium hydroxide as an acidic oxide.—The feeble acidic properties of aluminium hydroxide are evidenced by the solubility of the hydroxide in alkalies and by the formation of salts—aluminates—with the strong bases. The hydroxide H_3AlO_3 is called **orthoaluminic acid** when it is desired to emphasize its acidic nature The corresponding salts, $Al(OM')_3$, $Al(OH)(OM')_2$, $Al(OH)_2(OM')$, are orthoaluminates $Al(OH)_3 + 3NaOH = Al(ONa)_3 + 3H_2O$; $Al(OH)_3 + NaOH = AlO(ONa) + 2H_2O$ These compounds remain behind when the solutions are evaporated to dryness They also separate when alcohol is added to the solutions. Solutions of the aluminates furnish precipitates of the respective aluminates when salts of the alkaline earths are added $2NaAlO_2 + CaCl_2 = Ca(AlO_2)_2 + 2NaCl$ Salts corresponding with $NaAlO_2$ are considered to be derived from the acid $HAlO_2$, called **meta-aluminic acid**, which corresponds with the ortho acid less one molecule of water The minerals *spinel*—MgO Al_2O_3, or magnesium meta aluminate, $Mg(AlO_2)_2$—*chrysoberyl*—BeO Al_2O_3, or beryllium meta aluminate, $Be(AlO_2)_2$; *gahnite*—ZnO Al_2O_3, or zinc meta-aluminate, $Zn(AlO_2)_2$—are supposed to be meta aluminates which can be represented by the graphic formulæ

KO—Al=O	Mg<(O—Al=O)(O—Al=O)	Be<(O—Al=O)(O—Al=O)	Zn<(O—Al=O)(O—Al=O)
Potassium meta aluminate	Spinel	Chrysoberyl	Gahnite

Aluminates.—The aluminates are not very stable Their aqueous solutions are strongly alkaline on account of hydrolysis. They are decomposed by carbon dioxide with the precipitation of aluminium hydroxide $2NaAlO_2 + CO_2 + 3H_2O \rightleftharpoons 2Al(OH)_3 + Na_2CO_3$ Ammonium chloride produces a similar precipitate owing probably to the immediate hydrolysis of an unstable ammonium aluminate $Al(ONa)_3 + 3NH_4Cl \rightleftharpoons Al(ONH_4)_3 + 3NaCl$, which is completely hydrolyzed by water $Al(ONH_4)_3 + 3H_2O \rightleftharpoons 3NH_4OH + Al(OH)_3$. The aluminium hydroxide so obtained is a pulverulent powder not gelatinous like that precipitated from the acid solution of aluminium salts; it is also much less readily dissolved by acetic acid. The alumina of commerce has usually been precipitated from sodium aluminate, and it generally contains some sodium carbonate due to the imperfect washing of the precipitate

It is interesting to note that "intermediate oxides"—that is, oxides which can act both as acids and bases—must necessarily have both properties *feebly* developed because, in the language of the ionic hypothesis, the acidic and basic qualities depend on the presence of H and OH' ions, and both ions cannot be present in very great concentration in the same solution, owing to their tendency to unite and form water

Aluminium oxide, Al_2O_3.—Aluminium oxide, or alumina, occurs in nature as colourless crystalline corundum; and tinted with various metallic oxides as ruby, sapphire, amethyst, emery, etc Alumina is prepared as a white powder by the ignition of aluminium hydroxide, aluminium nitrate, or ammonia alum Alumina fuses at about 2000° Alumina is prepared in a crystalline condition by strongly heating a mixture of aluminium

fluoride and boric oxide $2AlF_3 + B_2O_3 = Al_2O_3 + 2BF_3$ Artificial rubies have been made by heating alumina with chromic oxide and boric oxide The latter acts as a flux and gradually volatilizes leaving behind the crystalline artificial "gem" When alumina is heated above about 800° an exothermal change takes place, the alumina changes in some way, for it then becomes almost insoluble in acids, its specific gravity rises rapidly from 2 8 to 4 0, and other physical properties change at the same time The change is supposed to be due to the formation of an allotropic modification of alumina. Similar remarks apply to the effects of high temperatures on ferric, chromic, and many other oxides When heated with reducing agents—potassium, sodium, calcium carbide, etc —alumina is reduced to the metal Bauxite is used in the manufacture of the so called "bauxite bricks," and for lining the bed of basic open hearth furnaces Fused bauxite or fused alumina is manufactured, sold as "alundum," "diamantine," etc, and used in the manufacture of abrasive and refractory materials.

§ 7 Gallium, Indium, and Thallium.

The rare metal gallium, Ga, was discovered by Lecoq de Boisbaudran in 1875 while studying a zinc blende from the Pyrenees, and named after Gallia, the Latin name of his country Indium, In, is another rare metal discovered in 1863 by T Reich and F Richter in a zinc ore from Freiberg Both elements were discovered by the spectroscope The spark spectrum of gallium contains two violet lines, and indium has a characteristic bright indigo blue line The latter element was named from its prominent indigo spectral line Gallium and indium metals are readily attacked by water, although indium slowly decomposes water at ordinary room temperatures Gallium and indium are attacked by nitric acid, whereas aluminium under the same conditions appears to be passive Gallium and indium are related to aluminium much as zinc is related to magnesium Aluminium, gallium, and indium form oxides R_2O_3 The hydroxides $R(OH)_3$ have weak acidic and basic properties All three elements form well-defined isomorphous ammonia alums. Unlike gallium chloride, $GaCl_3$, and aluminium chloride, $AlCl_3$, indium chloride, $InCl_3$, can be obtained by the evaporation of the aqueous solution at 100° with relatively little hydrolysis All three elements are trivalent, but indium also forms three chlorides $InCl$, $InCl_2$, and $InCl_3$

Thallium, Tl, was discovered by W Crookes in 1861 while studying the flue dust from a sulphuric acid chamber at Tilkerorde (Hartz mountains) Thallium occurs associated with pyrites in zinc ores, and in the mineral *crookesite*, a copper selenide containing 16 to 18 per cent of thallium, and 3 to 5 per cent of silver Thallium was discovered by the spectroscope Its spectrum has a characteristic green line—hence its name is derived from the Greek θαλλός (thallos), a green twig The physical properties of the metal closely resemble lead, and its compounds are related to aluminium, gallium, and indium, much as gold is related to the alkali metals, and mercury to zinc and cadmium Thallium forms a series of thallous salts similar in properties to mercurous and silver salts The thallic salts are not very stable, and they behave somewhat like the auric salts.

§ 8 The Relationships of Boron-Aluminium Family

The variations in the physical properties of these five elements with increasing atomic weight is indicated in the following table

TABLE XLVI.—PROPERTIES OF THE BORON-ALUMINIUM FAMILY

	Boron.	Aluminium	Gallium	Indium	Thallium
Atomic weight	11.0	27.1	69.9	114.8	204.0
Specific gravity	2.45	2.7	5.9	7.4	11.8
Atomic volume	4.5	10.0	11.8	15.5	17.3
Melting point	2200°	657°	30°	176°	285°

With the exception of boron and aluminium, the elements of this series are scarce and rare. The non-metallic characters predominate in boron. Boric oxide exhibits very feeble basic properties. The basic properties of the elements increase, and the acidic properties decrease with increasing atomic weights until thallium is reached. The trichloride, $TlCl_3$, for instance, is partially hydrolysed by water. When thallium is trivalent, its compounds resemble the other members of the group, but when univalent, thallium behaves like silver and the alkali metals. Thallium itself resembles lead.

§ 9 Scandium, Yttrium, Lanthanum, and Ytterbium

	Scandium, Sc	Yttrium, Y	Lanthanum, La	(Neo) Ytterbium, Yb
Atomic weight	44.1	89.0	139.0	172.0

The four rare elements, scandium, yttrium, lanthanum, and neo ytterbium, are related to the aluminium family. They are all triad elements. Their oxides are all of the type R_2O_3, and their halogen compounds RCl_3, etc. The hydroxides are all basic and insoluble in alkaline hydroxides. The basicity increases in passing from scandium to ytterbium. Scandium, for example, is a very weak base, while lanthanum forms the hydroxide, with the evolution of heat, by the direct action of water on the oxide. All the elements form stable carbonates, the halides are non-volatile, and are but slightly hydrolysed by water. They form double sulphates—$La_2(SO_4)_3.3K_2SO_4$—with the alkali sulphates, but these compounds are not alums. A. von Welsbach (1906) and G. Urbain (1907) found that what was previously considered to be ytterbium is really a mixture of two elements—ytterbium proper or neo ytterbium and a new element, called by Urbain, lutecium—from *Lutèce*, an old name for Paris. Lutecium has an atomic weight of 174. The relations between these elements and the aluminium family are often emphasized by the scheme shown in the margin.

```
    B
    |
    Al
   /  \
 Sc    \
  |    Ga
  Y     |
  |    In
 La     |
  |    Gd
 Yb     |
       Tl
```

Questions

1. What weights of sodium, zinc, and aluminium respectively would be required to yield 168 litres of hydrogen measured at N.T.P.? (Na = 23, Zn = 65.4, Al = 27).—*Aberdeen Univ.*

2 Give the preparation of pure aluminium oxide from bauxite and work out a similar method for preparing potassium chromate from chrome iron ore — *Amherst Coll, U S A*

3 Write the formulæ of the chief "alums" known Point out their characters as a class State and explain the principle they illustrate —*London Univ*

4 Compare the oxides of chromium with those of iron, of sulphur, and of aluminium —*Massachusetts Inst Technology, U S A*

5 Mallet determined the atomic weight of aluminium (1) by estimating the hydrogen evolved by the action of caustic soda on the metal, when 5 2632 grams of aluminium gave 5 2562 grams of water, (2) by analysis of the bromide, when 8 6492 grams of the bromide required 10 4897 grams of metallic silver for precipitation Required the atomic weight from (1) and (2) ($Ag = 107\ 66$, $Br = 79\ 75$, $O = 15\ 96$) —*Science and Art Dept*

6 Point out without using symbols the most marked features of resemblance and of difference in the chemical behaviour of the metals iron and aluminium and of their compounds —*Cambridge Senior Locals*

7 At 180° potash alum loses 43 67 per cent of water Point out the significance of this fact in deciding between the formulæ $AlK(SO_4)_2\ 12H_2O$, and $Al_2K_2(SO_4)_4\ 24H_2O$ —*London Univ*

8 What is the composition of borax and to what class of salts does it belong? Mention some examples of other salts of similar composition What is the action of a solution of borax on litmus?—*London Univ*

9 Into what classes can the following oxides be placed with reference to their behaviour towards acids and bases—calcium oxide, aluminium oxide, manganese dioxide, sulphur trioxide, nitrogen peroxide? State the reasons for your classification.—*London Univ*

10 What is an alum? Give the formulæ (*a*) ammonia alum, (*b*) potash alum, (*c*) chrome alum, (*d*) iron alum Describe the preparation of a specimen of any *one* What is the action of heat on (*a*)?—*London Univ*

11 What metals are capable of yielding alums, and what do you infer from these facts as to the mutual relations of these metals?—*Board of Educ*

CHAPTER XXXIV

The Platinum Metals

§ 1 Review of the Platinum Metals

The "platinum metals" include platinum, Pt, iridium, Ir, osmium, Os, palladium, Pd, rhodium, Rh, and ruthenium, Ru They occur in a metallic condition in gravels and sands associated together as mixtures or compounds along with magnetite, gold, chromite, etc, principally in Ural and Caucasus (Russia), and in smaller quantities in California, Sumatra, New Granada, Brazil, Australia, etc The platiniferous sands and gravels are washed as in the case of alluvial gold "Platinum concentrates" consist of rounded grains or flattened scales containing approximately the following percentage composition

Platinum	Iridium	Rhodium	Palladium	Gold	Copper	Iron	Osmiridium	Sand
76 4	4 3	0 3	1 4	0 4	4 1	11 7	0 5	1 4

The *osmiridium* is a native metallic alloy containing approximately

Platinum	Iridium	Rhodium	Osmium	Ruthenium
10 1	52 5	1 5	27 2	5 9

with traces of palladium, copper, and iron

The metals are greyish white and lustrous They all melt at a high temperature They are not acted on by air or oxygen at ordinary temperatures Osmium alone burns when strongly heated, forming the tetroxide OsO_4, the others are scarcely affected, chemically, at any temperature Palladium dissolves in hot nitric acid, but the other metals are scarcely affected by hot acids Aqua regia attacks osmium, forming osmium tetroxide, OsO_4, platinum forms the tetrachloride, $PtCl_4$, ruthenium is slowly dissolved, while iridium and rhodium are not appreciably attacked. The metals are readily reduced from their compounds, which fact probably accounts for their occurrence free in nature. The metals fall naturally into two groups with nearly equal molecular weights The *light platinum metals* include ruthenium, rhodium, and palladium, the *heavy platinum metals* include osmium, iridium, and platinum Palladium is related with silver, and platinum with gold, as indicated in Table XLVII (p 641)

Extraction of the metals—The gold can be removed from the platinum concentrates by the amalgamation process About 1860, the platinum, contaminated more or less with other metals, was extracted by a smelting process, to day, a wet process is used Details of the process are a "trade secret" In a general way it may be said that the concentrates are digested with aqua regia The insoluble residue contains sand

and osmiridium Osmium and ruthenium form volatile oxygen compounds which can be easily removed from the solution by distillation When the solution of crude platinum in aqua regia is treated with ammonium chloride, a precipitate containing platinum and iridium compounds is obtained from which the metals are obtained by ignition The mother liquid is worked over for palladium and rhodium The further separation of the platinum metals from one another is a difficult and laborious operation because the properties of the metals are so much alike, and because the behaviour of the salts of one element is modified by the presence of others Thus, iridium does not dissolve in aqua regia, but if iridium be alloyed with platinum, some iridium passes into solution when the alloy is digested in aqua regia

TABLE XLVII —PROPERTIES OF THE PLATINUM METALS

	Light				Heavy			
	Ru	Rh	Pd	Ag	Os	Ir	Pt	Au
Atomic weight	101 7	103 0	106 0	107 88	191 0	193 0	194 8	195 7
Specific gravity	12 26	12 1	11 9	10 6	22 47	22 38	21 45	19 31
Atomic volume	8 3	8 5	8 9	10 1	8 5	8 6	9 1	10 1
Melting point	c 2000°	1650°	1549°	962°	2300°	2000°	1755°	1064°
Boiling point	2780°	2750°	2820°	1955°	2950°	2850°	2650°	2200°
Valency	3, 8	2, 3, 4	2, 4	1, 2, 3	2,3,4,8	2, 3, 4	2, 4	1, 3

History —There is supposed to be a reference to platinum in Pliny under the name "aluta" The term "platina del Pinto" for a white metal resembling silver, has been for a long time in general use by the Spaniards in South America "Platina" is the diminutive form of the Spanish *plata*, silver, and "Pinto" has reference to the river where it was discovered. At one time its export from South America was forbidden by the Spanish Government, who ordered it to be thrown into the sea to prevent its being used for adulterating gold In 1788, the Spanish Government bought it for about 8*s* per lb, presumably for adulterating gold It is now worth over £100 per lb Platina del Pinto attracted the attention of Antonio de Ulloa at Choca (Columbia) in 1735 It was brought to Europe in 1735 by C Wood, and R Watson described its properties in 1750 It attracted much attention at the time Before 1823, most of the platinum in commerce came from South America Platinum was discovered in Ural in 1819, and in 1824 Russia began exporting platinum, since that time, most of the platinum of commerce has come from that source

Osmium and iridium were discovered by S Tennant, 1802 to 1803, rhodium and palladium by W H Wollaston, 1803 to 1804, and ruthenium by A Claus in 1845 All these metals were found during the study of native platinum "Osmium" is named from the Greek ὄσμη (osme), a smell, "iridium" is named from the Greek ἶρις (iris), a rainbow, from the varying tint of its salts, "rhodium" is named from the Greek ῥόδον (rodon), a rose, from the rose-red colour of its salts, "palladium" is named after the planet Pallas, discovered the same year as palladium, 1802, "ruthenium" is named after *ruthen*, for Russia

§ 2 The Chlorides and their Complex Acids

✓ **Platinum tetrachloride, $PtCl_4$**—Platinum dissolves in aqua regia If the solution be evaporated to dryness, and the residue gently heated, a solution of the residue in hot water deposits reddish brown crystals of $PtCl_4.5H_2O$ on cooling The anhydrous chloride, $PtCl_4$, can be made by drying the crystals over sulphuric acid and warming them in a current of chlorine The tetrachloride decomposes into the metal and chlorine at about 590° Chlorides of all six platinum metals of the type $PtCl_4$ are known. Palladium tetrachloride is not known in a free state, but double chlorides with potassium, etc , are known

Chloroplatinates —If platinum chloride be crystallized from a solution acidified with hydrochloric acid, or if an aqua regia solution of the metal be evaporated a number of times with an excess of hydrochloric acid to drive off the nitric acid, reddish brown deliquescent crystals of the complex acid $H_2PtCl_6.6H_2O$ are formed This substance—the "platinum chloride" of commerce—is really hydrochloroplatinic acid The acid is dibasic, and it forms a characteristic series of complex salts—the chloroplatinates. Potassium chloroplatinate, K_2PtCl_6, for example, is a yellow crystalline precipitate made by adding the acid to a solution of potassium chloride While the solubilities of the normal alkali chlorides in water *increase* in passing from lithium to cæsium, the chloroplatinates *decrease* in solubility in passing from lithium to cæsium For instance, 100 c c of water at 10° dissolves, in grams

Li_2PtCl_6	Na_2PtCl_6	K_2PtCl_6	Rb_2PtCl_6	Cs_2PtCl_6
Very soluble	1 15	0 90	0 15	0 05

The solubility of ammonium chloroplatinate, $(NH_4)_2PtCl_6$, is 0 6 at 10°, and it thus comes between potassium and rubidium chloroplatinates. The fact that the sodium salt is fairly soluble in 80 per cent. alcohol, while the potassium salt is almost insoluble, enables a mixture of the chloroplatinates of sodium and potassium to be separated The ammonium salt behaves like the potassium salt During the electrolysis of ordinary salts—silver nitrate, potassium chloride, etc —the metal is deposited on the cathode, with the chloroplatinates, the platinum is deposited on the anode Again, silver nitrate precipitates Ag_2PtCl_6, not AgCl, thus confirming the deduction that "$PtCl_6$" is a bivalent complex acid radicle or that the solution of the acid furnishes the ions $2H^{\cdot}$ and $PtCl_6''$ on electrolysis The constitution of the chloroplatinates will be discussed later

Platinum dichloride, $PtCl_2$—If hydrochloroplatinic acid be heated between 250° and 300°, it furnishes grey granular powder of platinum dichloride, $PtCl_2$, insoluble in water, at higher temperatures, it decomposes into platinum and chlorine Platinum dichloride is also formed when platinum is heated to about 582° in chlorine gas All six metals of the platinum series form salts of the type $PtCl_2$ Palladious iodide, PdI_2, is precipitated as a black insoluble powder when potassium iodide is added to solutions of palladious chloride. This reaction is used sometimes for the separation of iodine from the other halogens, since the other halogen salts of palladium are soluble Carbon monoxide unites with platinous chloride forming carbonyl platinous chlorides, $CO.PtCl_2$, $2CO.PtCl_2$, $3CO.2PtCl_2$

Chloroplatinites.—When platinum dichloride is digested with hydrochloric acid, it furnishes a reddish-brown solution which is supposed to contain hydrochloroplatinous acid, H_2PtCl_4. The acid has not been isolated, but the salts—chloroplatinites—are formed by treating the solution with, say, potassium chloride. Potassium chloroplatinite, K_2PtCl_4, forms rose red crystals. The same salt is formed by reducing potassium chloroplatinate with moist cuprous chloride, $CuCl$. Potassium chloroplatinite is used in platinum printing in photography. This chloride is reduced to metallic platinum by ferrous oxalate. Palladium forms a similar series of chloropalladites.

Platinum-ammonia compounds.—The platinum metals behave in a peculiar manner with ammonia. Thus, when ammonia is added to a solution of platinum tetrachloride, $PtCl_4$, in hydrochloric acid, a green precipitate is formed. If the mixture be boiled, a green insoluble compound $PtCl_2.4NH_3 + H_2O$, called Magnus' green salt, is formed and $PtCl_2.2NH_3$ remains in solution. If the precipitate be heated to 250°, a yellow crystalline substance sparingly soluble in water is formed, $PtCl_2.2NH_3$. Both compounds can be oxidized with chlorine to $PtCl_4.2NH_3$. These two compounds may be taken to represent two well defined series of platinum ammonia compounds. One series is derived from $PtCl_2$ and the other from $PtCl_4$. These will be discussed very shortly.

§ 3. The Oxides and Hydroxides.

When a solution of potassium chloroplatinite or of platinous chloride is treated with an alkaline hydroxide, platinous hydroxide, $Pt(OH)_2$, is precipitated as a black powder. It is soluble in the haloid acids—hydrochloric and hydrobromic acids—and in sulphurous acid, but not in the other oxy-acids, and thus forms the corresponding platinous salts. The hydroxide is decomposed into the metal and platinum dioxide, PtO_2, by boiling alkaline hydroxides: $2Pt(OH)_2 = PtO_2 + Pt + 2H_2O$. When gently ignited, platinous hydroxide forms the corresponding platinous oxide, PtO, as a dark powder insoluble in water and in most acids. It is doubtful if IrO has been made.

When a boiling solution of potassium hydroxide is added to a solution of platinum tetrachloride, and the precipitated platinic hydroxide, $Pt(OH)_4$, is washed with acetic acid to remove the potash, a yellowish powder is obtained which dissolves in acids, forming platinic salts, and in bases forming a series of salts called the platinates. For instance, with sodium hydroxide, yellow crystals of sodium platinate, $Na_2O.3PtO_2.6H_2O$, are obtained. Hence platinic hydroxide is an acidic and a basic compound. Platinic hydroxide, $Pt(OH)_4$, is a type of similar compounds formed by the whole six of the platinum metals. The hydroxides when heated form dark grey powders of the dioxide—*e.g.* PtO_2, IrO_2, etc.

Ruthenium, osmium, iridium, and rhodium form sesquioxides: Ru_2O_3; Os_2O_3, Ir_2O_3, Rh_2O_3. Ruthenium and osmium form compounds corresponding with the trioxides RuO_3 and OsO_3. A more or less impure IrO_3 has been made. Thus, potassium ruthenate, K_2RuO_4, and potassium perruthenate, $KRuO_4$, call to mind potassium manganate and permanganate. Ruthenium and osmium also form tetroxides of the type RuO_4 and OsO_4 respectively. These compounds represent the highest known state of oxidation of any

single metal The nearest approach to this state of oxidation occurs with perchloric and permanganic acids The tetroxides dissolve in water but the solutions are not acid (1) they are neutral to litmus, (2) do not decompose carbonates, and (3) form crystalline salts The acids show no signs of hydrolysis The term "osmic acid" for osmium tetroxide is thus a misnomer Both tetroxides, RuO_4 and OsO_4, melt at a low temperature, about +40°, and boil at about 100° giving irritating vapours Osmium tetroxide vapours are very poisonous, and seriously injure the eyes They decompose on further heating into the dioxide and oxygen The solutions are reduced by organic matters and the finely divided metal is precipitated.

§ 4 The Properties and Uses of Platinum

Platinum is a greyish white metal with a brilliant lustre It is harder than copper, silver, or gold It is ductile and malleable, and usually comes on the market in the form of foil or wire. Platinum has also the valuable quality that it softens like iron before melting, so that like iron it can be welded Platinum melts between 1750° and 1755°, and boils at about 2450° Platinum and rhodium do not volatilize appreciably at 900°, but at 1300° volatilization can be detected Appreciable quantities of the metals palladium, iridium, and ruthenium volatilize at 900°, and at 1300° the effect is very marked Iridium is readily oxidized to a volatile sesquioxide when heated just below 1000°, but it is doubtful if platinum is oxidized below 1300° Molten platinum, like molten silver, absorbs oxygen which is given off as the molten metal cools, hence it is liable to "*spitting*". Platinum is not attacked by pure hydrofluoric, hydrochloric, nitric, and sulphuric acids. It is readily dissolved by aqua regia and by solutions containing chlorine, see "Gold." When platinum is alloyed with silver, copper, lead, zinc, etc, it is attacked and partly dissolved by nitric acid, probably forming a platinum nitrate

The high fusing temperature, and the fact that platinum is not attacked by air and strong acids enables it to be used in the manufacture of apparatus—dishes, crucibles, stills, etc—for many chemical operations which could not be readily performed with apparatus made from other available metals The unfortunate steady advance in the price will lead to the use of gold crucibles for many purposes The analysis of many minerals could not be so readily conducted as at present if it were not for the valuable qualities of platinum Platinum is attacked by alkalies, nitrates, cyanides, and phosphates under reducing conditions With phosphorus it forms platinum phosphide, with sulphur, platinum sulphide, PtS, with sulphur and dry alkali, platinum disulphide, PtS_2, with arsenic, platinum arsenide, Pt_2As_3 An arsenide called *sperrylite*, $PtAs_2$, associated with nickel sulphide occurs at Sudbury (Ontario) Platinum also alloys directly with metals like lead, silver, zinc, etc, but not mercury Hence platinum crucibles must not be heated with these metals Carbon alloys with platinum forming a brittle platinum carbide, and hence platinum crucibles must not be heated in smoky flame

Platinum has nearly the same coefficient of expansion as glass, and platinum wires can be fused in glass so as to make gas tight joints. Platinum is also a good conductor of electricity, and large quantities are

used in the electric light industry Short pieces of platinum wire are fused into the glass at the base of the bulb, and connected with the filament inside. The bulb is then exhausted and sealed. The platinum wires outside are then put in communication with the wire carrying the current The filament is thus heated under reduced pressure to form the "incandescent electric light" Platinum is used in dentistry, photography, in jewellery, and in making scientific and surgical instruments, etc

Platinum iridium alloys are hard and elastic, malleable and ductile, and less fusible than platinum. If more than 20 per cent of iridium be present, the alloys are exceedingly difficult to work An alloy of 10 per cent iridium and 90 per cent platinum was chosen by the International Committee on Weights and Measures for preserving the standards of length and weight Platinum-iridium wire with platinum wire are used as thermocouples for temperatures up to 1000°, and platinum-rhodium wires are used with platinum in a similar way for temperatures up to 1400° Commercial platinum has 2 per cent of iridium, and it appears to gradually lose this constituent when heated to a high temperature The result is that platinum crucibles made from commercial platinum lose in weight every time they are heated for some time in the gas blowpipe This is a source of annoyance The high fusing temperature of osmium has led to its use for the manufacture of filaments for incandescent electric lamps—"osmium lamps" An alloy of iridium and osmium is used for tipping gold nibs on account of its hardness The alloy is called *iridosmine* or *osmiridium* Palladium is used for absorbing hydrogen, for the detection of carbon monoxide, and for the separation of iodine as indicated above Osmium tetroxide is used for staining and hardening organic tissues in histology

When platinum is precipitated from solutions of the tetra-chloride by reducing agents, a velvet black powder called platinum black is obtained, when ammonium chloroplatinate is calcined, the metal remains behind as a spongy mass called spongy platinum, and if asbestos be soaked in a solution of platinum chloride and ignited, the asbestos permeated with platinum is called platinized asbestos Platinum sponge, platinum black, and platinized asbestos absorb large quantities of oxygen gas, and they can then be used as oxidizing agents Platinum black can absorb 100 times its volume of oxygen and 110 times its volume of hydrogen. Palladium black absorbs about 900 times its volume of hydrogen This property of occluding gases is shown in a less marked degree by iron, nickel, and cobalt, as well as by copper, gold, and silver Spongy platinum will cause a mixture of hydrogen and oxygen to unite with explosion, spongy palladium without explosion A jet of hydrogen directed on to finely divided platinum will cause the platinum to glow and finally ignite the jet of gas Alcohol dropped on to iridium black takes fire Similarly coal gas can be ignited by spongy platinum, and this property is utilized in making the so-called "self-lighting Bunsen's burners" The catalytic properties of the finely divided platinum metals are used in some industries for promoting chemical changes, *e.g* the contact process for sulphuric acid

§ 5 Werner's Views on Valency, and on the Constitution of Molecular Compounds

The attempt to distinguish molecular from atomic compounds, by structural formulæ based upon ordinary valencies deduced from the

manifestations of the simple "atomic compounds" discussed in previous chapters, has not been successful Some of the elements involved in the formation of the molecular compounds manifest higher valencies than the numbers deduced from the simpler, more numerous, and more stable compounds. A. Werner's hypothesis—1893 *et seq*—seems to give a clearer insight into the constitution of double salts, complex salts, crystalline hydrates, etc, than any yet propounded Although it is certain that Werner's hypothesis has not assumed its final form, yet it promises to banish the conception of molecular compounds as something specifically distinct from atomic compounds

Residual Affinity—According to Werner, when the combining capacity of an atom, as defined by the theory of valency, is exhausted, the atoms still possess a "particular kind of affinity," which enables them to form molecular complexes, corresponding with Berzelius' "compounds of higher orders," p 306 In other words, simple or primary molecules may possess a residual affinity which enables them to unite together and form more complex stable compounds Thus, the sulphur atom in sulphur trioxide, the oxygen atom in water, the chlorine atom in hydrogen chloride, the nitrogen atom in ammonia, the gold atom in auric chloride, the platinum atom in platinic chloride, etc, all possess residual affinity which permits these molecules to unite additively with other molecules Residual affinity appears to play a *rôle* similar to ordinary chemical affinity, but the new manifestations of valency differ from the manifestations of ordinary valency in that they bind entirely different radicles. For instance, residual affinity does not lead to the combination of univalent radicles as defined by the doctrine of valency This does not mean that the mode of action of the two kinds of affinity is different, since both are in many ways similar "Nevertheless," says Werner, "it appears at present desirable to preserve the difference because the doctrine of valency is yet in a transitional stage, and hence it is judicious to construct sharply defined concepts." Accordingly, Werner distinguishes two kinds of valency

1 Chief or primary valency which represents those manifestations of chemical affinity which enable the combining capacities (valencies) of the elements to be expressed in terms of hydrogen atoms or their equivalents, *e g* Cl—, Na—, NO_2—, CH_3—,

2 Auxiliary or secondary valency which represents those manifestations of chemical affinity which are able to bring about the stable union of molecules as if the molecules were themselves radicles able to exist as independent molecules, *e g* H_2O—, NH_3—, HCl—, $CrCl_3$—,

Co-ordination number—When the binding capacity of an elementary atom (primary valency) appears exhausted, Werner assumes that the atom can still link up with other molecules (secondary valency), and build up more complex molecules. There is, however, a limit to the binding capacity of both primary and secondary valencies The number which represents the joint effect of both the primary and the secondary valencies is called the "co ordination number" The co-ordination number of an atom is the maximum number of atoms, radicles, or molecular groups—independent of their valencies—which can be directly linked with a central atom The co ordination number of an atom can be determined from compounds in which the maximum number of atoms,

radicles, or molecular groups, linked with a central atom, are known. The co-ordination number of most atoms, curiously enough, is six; in a few cases it is four; and with molybdenum and the addition products of the chlorides of the alkaline earths, the co-ordination number appears to be eight. The fact that the co-ordination number for so many elements is six, and is generally independent of the nature of the co-ordinated groups, has made Werner suggest that the number is decided by available *space* rather than affinity and that six is usually the maximum number which can be fitted about the central atom to form a stable system. Consequently the co-ordination number represents a property of the atom which enables the constitution of "molecular compounds" to be referred back to actual linkings between definite atoms. A molecular compound is primarily formed through the agency of secondary valencies; and, just as primary valencies determine the number of univalent atoms or their equivalent which can be linked to a central atom, so secondary valencies determine the number of molecules which can be attached to the central atom. The secondary valency is often active only towards definite molecular complexes, and hence the formation of additive compounds with other molecular complexes does not occur. Accordingly, the number of secondary valencies which are active towards different molecules is not always the same. To illustrate by example:

Ammonium chloride.—When it is desired to emphasize the distinction between primary and secondary valencies, Werner recommends using a continuous line for the former, and a dotted line for the latter. The nitrogen atom of ammonia, NH_3, has an unsaturated secondary valency, and the hydrogen or chlorine atom in hydrogen chloride, HCl, has likewise an unsaturated secondary valency. The formation of ammonium chloride is therefore illustrated by the scheme: $H_3N + HCl = H_3N \cdots HCl$. The dotted line represents the auxiliary valency joining the hydrogen atom of HCl with the nitrogen atom of NH_3. The co-ordination number of the nitrogen atom is here 4. It is not likely that one of the hydrogen atoms in ammonium chloride is "linked with a greater amount of affinity than the other three," and very probably, there is a state of equilibrium in which the affinity is distributed over all the hydrogen atoms, and a complex radicle is formed in which each of "the four atoms of hydrogen is united to the nitrogen atom by the same amount of affinity." Hence Werner writes the structural formula of ammonium chloride:

$$\begin{bmatrix} H & & H \\ & N & \\ H & & H \end{bmatrix} Cl$$

The practice of assuming an increased valency for nitrogen when ammonia unites with hydrogen chloride, says Werner, if consistently carried out would make antimony tervalent in antimony trichloride, and quinquevalent in $SbCl_3 \cdot KCl$, etc. Bivalent, Fe, in ferrous cyanide, $FeCy_2$, would become decivalent in potassium ferrocyanide, K_4FeCy_6.

Sulphuric acid.—The formation of sulphuric and chlorosulphuric acids by the union of sulphur trioxide with water and hydrogen chloride respectively is brought about by the secondary valencies as indicated in the schemes: $O_3S + OH_2 = O_3S \cdots OH_2$; and $O_3S + ClH = O_3S \cdots ClH$. *When one of the reacting molecules contains double-linked atoms, the secondary valencies may not be sufficiently strong to preserve the integrity of*

the new molecule, and the atoms of the addition product may be rearranged For example, this is the case with sulphur trioxide Thus

$$\begin{array}{l}O\\O\!=\!S\\O\end{array}\!\!>\ \cdot OH_2 \text{ passes into } \begin{array}{l}O\\O\end{array}\!\!>\!S\!<\!\begin{array}{l}OH\\OH\end{array}, \text{ and } \begin{array}{l}O\\O\!=\!S\\O\end{array}\!\!>\ ClH \text{ into } \begin{array}{l}O\\O\end{array}\!\!>\!S\!<\!\begin{array}{l}OH\\Cl\end{array}$$

The change in the type of the compound is due to an intramolecular rearrangement, but such a change may not occur if the secondary valency is sufficiently strong and the addition product is stable

Platinum-ammines —What has just been suggested appears to be applicable with the analogous reactions $Cl_4Pt + 2NH_3 = Cl_4Pt\ (NH_3)_2$, and $Cl_4Pt + 2KCl = Cl_4Pt\ (ClK)_2$ Werner represents the two latter compounds by the formulæ

$$[Pt(NH_3)_2Cl_4] \qquad\qquad [PtCl_6]K_2$$

All four chlorine atoms can be removed from the first compound without disturbing the ammonia molecules, and consequently the chlorine atoms do not act as intermediate links binding the NH_3 molecules to the platinum, as they would in, say, $Cl_2Pt(Cl\ NH_3)_2$ It is therefore inferred that the NH_3 molecules are directly attached to the platinum atom Again, no difference has been detected in the chemical behaviour of the four chlorine atoms This would not be the case if the two ammonia molecules were intermediate links between two of the chlorine atoms, and the central atom of platinum, as would be the case in, say, $Cl_2Pt(NH_3\ Cl)_2$ Hence, in all probability, the six groups are all attached directly to the platinum Consequently, Werner writes

$$\begin{array}{l}Cl\\Cl\\Cl\\Cl\end{array}\!\!>\!Pt\!<\!\begin{array}{l}NH_3\\NH_3\end{array} \qquad\qquad \begin{array}{l}Cl\\Cl\\Cl\\Cl\end{array}\!\!>\!Pt\!<\!\begin{array}{l}ClH\\ClH\end{array}$$

The latter formula has been established in a similar manner to the former

A study of the platinum ammines shows that they can be arranged in two well defined series. One series is derived from platinic chloride, $PtCl_4$, and the other from platinous chloride, $PtCl_2$ The co ordination number of the former is six, and of the latter, four Thus

1 *Platinum-ammines derived from platinous chloride*—$PtCl_2$

1	Tetrammineplatinous chloride	$[Pt(NH_3)_4]Cl_2$
2	Chlorotriammineplatinous chloride	$[Pt(NH_3)_3Cl]Cl$
3	Dichlorodiammineplatinum (two isomers)	$[Pt(NH_3)_2Cl_2]$
4	Potassium trichloroammineplatinite	$[Pt(NH_3)Cl_3]K$
5	Potassium tetrachloroplatinite	$[PtCl_4]K_2$

2 *Platinum-ammines derived from platinic chloride*—$PtCl_4$

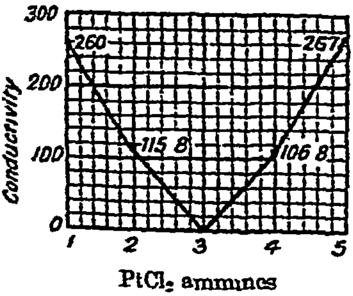
1	Hexammineplatinic chloride	$[Pt(NH_3)_6]Cl_4$
2	Chloropentammineplatinic chloride	$[Pt(NH_3)_5Cl]Cl_3$
3	Dichlorotetrammineplatinic chloride	$[Pt(NH_3)_4Cl_2]Cl_2$
4	Trichlorotriammineplatinic chloride	$[Pt(NH_3)_3Cl_3]Cl$
5	Tetrachlorodiammineplatinum (two isomers)	$[Pt(NH_3)_2Cl_4]$
6	Potassium pentachloroammineplatinate	$[Pt(NH_3)Cl_5]K$
7	Potassium hexachloroplatinate	$[PtCl_6]K_2$

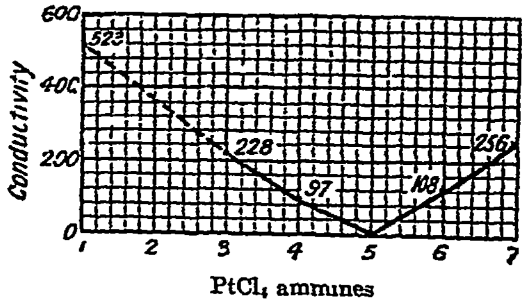
The simple or compound radicles which form the complex represented within the square brackets, are directly united with the central atom of platinum The complex takes part in chemical reactions as if it were one individual radicle The basic ammonia in the complex can be successively replaced by acidic radicles—Cl Br, NO_3, CO_3, SO_4, etc —until

the complex becomes acidic instead of basic and the platinic ammine complexes finally pass from electro-negative (basic) radicles to electropositive (acidic) radicles Potassium chloroplatinate is the limit of the platinic ammines and potassium chloroplatinite is the limit of the platinous ammines. It will be obvious that an enormous number of derivatives are conceivable

Nomenclature of the metal ammines —Werner s system of naming the metal-ammonia compounds has been almost universally adopted The constituents of the complex are taken first, and of these, the acid radicles with the suffix "o" come first, then follow any groups which behave like ammonia, e.g H_2O is called "aquo", NO_2, "nitrito" or "nitro", NO_3, "nitrato", CO_3, "carbonato", SO_3, "sulphito", etc. And lastly, preceding the metal itself, the ammonia molecules are designated "ammines," and spelt with a double "m" to distinguish the word from the "amines" or substituted ammonias The prefixes di, tri indicate the number of each The whole is written as one word Examples appear in the above list

The valency of the metal ammines.—The valency of the complex is numerically equal to the difference between the ordinary valency of the central atom and the number of negative (acidic) elements or groups attached to the metal Thus, the normal valency of platinum in the first of the above series is 4 hence the valency of $[Pt(NH_3)_5Cl]$, with





FIGS. 225 and 226 —The Electrical Conductivities of the Platinum-ammine Derivatives (The abscissæ refer to the numbers in the above tables)

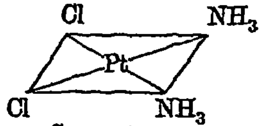
one negative (acidic) group "Cl," will be 3, this means that the complex in question acts as a tervalent electropositive (basic) radicle, and it can unite with three univalent electro-negative (acidic) radicles. The valency of $[Pt(NH_3)Cl_5]$ with five negative (acidic) groups, "Cl" will be —1 This means that the complex under consideration will act as a univalent electro-negative (acidic) radicle, and it can accordingly unite with one electropositive (basic) radicle like potassium, sodium, etc. If the valency of the acidic radicles in the complex are numerically equal to the normal valency of the central atom, the complex will be nullvalent This is the case, for instance, with the complex $[Pt(NH_3)_2Cl_4]$

Properties of the metal ammines—The nullvalent ammine bases are non electrolytes, they do not conduct electricity In the other ammine bases the complex forms one ion which is either electropositive (basic), and therefore a cation, or else electronegative (acidic), and therefore an anion. During electrolysis, the components of the complex are not disturbed The molecular conductivities of the ammine derivatives of $PtCl_2$ at 1000 litres dilution are indicated in Fig 225, the conductivities of the derivatives of $PtCl_4$ are indicated in Fig 226, the second derivative,

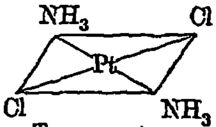
$[Pt(NH_3)_5Cl]Cl_3$, is not known The electrical conductivities of these compounds correspond with the "ions" obtained on electrolysis, as indicated by Werner's formulæ in the above tables

The analytical reactions of each base are characteristic of the complex as a whole, and of the radicles associated with the complex—indicated outside the square brackets in the above formulæ Thus, with the cobalt ammines, cobalt tervalent, all the bromine in $[Co(NH_3)_6]Br_3$ is precipitated by silver nitrate, in $[Co(NH_3)_5Br]Br_2$ only two thirds of the total bromine is precipitated by silver nitrate, and in $[Co(NH_3)_4Br_2]Br$, only one third of the total bromine is precipitated, and in $[Co(NH_3)Br_3]$ none of the bromine is precipitated

Isomerism of the ammines—The phenomenon of isomerism occurs with some of the ammines. Thus, croceo cobaltic chloride and flaveo-cobaltic chlorides have the same ultimate composition, $[Co(NH_3)_4(NO_2)_2]Cl$ One forms golden yellow solutions—*flavus* (golden yellow), and the other saffron coloured solutions—*κρόκος* (crocos), saffron Similarly, there are two isomers of dichlorodiammineplatinum and two isomers of tetrachloro diammineplatinum In the former, $[Cl_2Pt(NH_3)_2]$, the four radicles are attached to the central atom of platinum in pairs If the four groups were attached in space, say at the angular points of a regular tetrahedron, isomerism could hardly be expected because the four groups could be interchanged without altering their relations one with another [1] Hence it is inferred that the groups are arranged about the central atom of platinum in one plane The resulting isomerism can be graphically illustrated by the schemes



Cis position



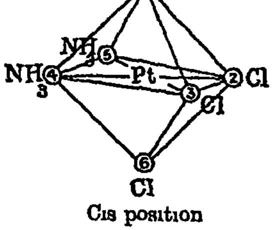
Trans position

Or by the more usual type of formulæ

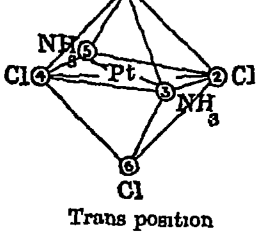
$$\begin{matrix}Cl\\Cl\end{matrix}>Pt<\begin{matrix}NH_3\\NH_3\end{matrix} \qquad \begin{matrix}NH_3\\Cl\end{matrix}>Pt<\begin{matrix}Cl\\NH_3\end{matrix}$$

Cis position. Trans position

The two isomers of $[Pt(NH_3)_2Cl_4]$ can be represented by



Cis position



Trans position

[1] It is not legitimate to assume that the absence of isomerism in methylene chloride, CH_2Cl_2, proves that the four hydrogen and chlorine atoms are distributed in space uniformly about a central carbon atom The fact that no isomerism has hitherto been discovered may also prove that there is *only one stable* configuration for the group CH_2Cl_2.

The isomerism of other ammines can be illustrated in a similar manner. If the corners of the octahedral figure be always numbered 1 to 6 as shown in the diagram, the relative positions of the acidic or basic radicles can be indicated by numbers. Assuming that the diagrams correctly represent the relative positions of the radicles, the cis compound is called the 2 3 tetrachlorodiammineplatinum, and the trans compound the 2 4-tetrachlorodiammineplatinum.

Cobalt-ammines.—Tervalent cobalt forms an important series of ammines. The so called luteo-cobaltic chloride $[Co(NH_3)_6]Cl_3$ is a hexamminecobaltic chloride, and it is formed in reddish-yellow prisms (luteus yellow), when a solution of cobaltous chloride containing ammonium chloride and ammonia is exposed to the oxidizing action of the air, or bromine, lead peroxide, etc. If an ammoniacal solution of cobaltous chloride be exposed to the oxidizing action of the air, roseo cobaltic chloride, or aquopentamminecobaltic chloride, $[Co(NH_3)_5H_2O]Cl_3$, is formed; if this solution be warmed, purpureocobaltic chloride or chloropentamminecobaltic chloride, $[Co(NH_3)_5Cl]Cl_2$, is formed; and when this is exposed to the action of nitrous acid, croceocobaltic chloride or nitritopentamminecobaltic chloride, $[Co(NH_3)_5NO_2]Cl_2$, is formed. Most of the 2000 known cobalt ammino compounds can be referred to one of the following seven series. Let A represent NH_3, H_2O, etc.; R represent the halogens, NO_2, NO_3, CO_3, Cy, etc.; and M a basic radicle univalent—K, Na, etc.

TABLE XLVIII.—COBALTAMMINES

	Type	Example—Werner's systematic name	Formula	Old name
I	$[CoA_6]R_3$	Hexamminecobaltic chloride	$[Co(NH_3)_6]Cl_3$	Luteocobaltic chloride
II	$[CoA_5R]R_2$	Nitritopentammine cobaltic chloride	$[Co(NH_3)_5NO_2]Cl_2$	Xanthocobaltic chloride
III	$[CoA_4R_2]R$	Dichlorotetrammine cobaltic nitrate	$[Co(NH_3)_4Cl_2]NO_3$	Chloropraseoco baltic nitrate
IV	$[CoA_3R_3]$	Trinitritotriammine cobalt	$[Co(NH_3)_3(NO_2)_3]$	——
V	$[CoA_2R_4]M$	Ammonium tetranitrito diamminecobaltate	$[Co(NH_3)_2(NO_2)_4]K$	Erdmann's salt
VI	$[CoAR_5]M_2$	Potassium pentanitrito amminecobaltate	$[Co(NH_3)(NO_2)_5]K_2$	——
VII	$[CoR_6]M_3$	Potassium hexanitrito cobaltate	$[Co(NO_2)_6]K_3$	Potassium co baltinitrite

Numerous derivatives of most of the classes are known, and an enormous number are possible, *e.g.* over a hundred members of the first class have been isolated. Potassium cobalticyanide, $[CoCy_6]K_3$, belongs to the seventh group. It is formed when a solution of a cobalt salt is warmed with an excess of potassium cyanide while exposed to the air. The cobaltous cyanide which first separates as a dirty brown precipitate forms the complex salt with the excess of potassium cyanide. The reaction is usually written $CoCy_2 + 4KCy = K_4CoCy_6$. According to Werner, this compound is $[CoCy_6]K_4$. This is oxidized to potassium cobalticyanide, $[CoCy_6]K_3$, on exposure to the air. Solutions of sodium hypobromite or hypochlorite

CHAPTER XXXV

The Oxides of Carbon

§ 1 Carbon Dioxide—Preparation

Molecular weight $CO_2 = 44$ Melting point, $-57°$ (under pressure), sublimes at $-78.2°$, critical temperature, $+31°$ Relative vapour density ($H_2 = 2$), 43.97, (air = 1) 1.529

Carbon dioxide is produced when carbon burns in the presence of an excess of oxygen Similar remarks apply to the combustion of many carbon compounds If a beaker be held over a candle flame for a few minutes to collect some of the products of combustion, and lime-water be then poured into the beaker, or if a candle be allowed to burn in a cylinder loosely covered with a glass plate, and lime water be added, the formation of a turbid solution is strong circumstantial evidence that carbon dioxide is present The production of a turbidity in clear lime-water is a characteristic test for carbon dioxide

Laboratory methods —Carbon dioxide is generally made in the laboratory by the action of hydrochloric acid upon calcium carbonate—marble, limestone, or chalk The action is represented in symbols $CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$ Calcium chloride is a by-product of the action Fragments of marble are placed in a Woulfe's bottle, Fig 9, p 43, with a quantity of water Concentrated hydrochloric acid is added by means of a funnel tube The gas can be collected, like hydrogen over water, or, unlike hydrogen, it can be collected by placing the delivery tube in an empty gas cylinder closed end downwards. The gas is so heavy that it displaces the lighter air upwards out of the jar—hence the term, *collecting the gas by the upward displacement of air* The gas so collected may contain a little air It is easy to test if the jar is full of gas because a lighted taper put down into the jar will be extinguished when it meets the carbon dioxide as completely as if it had been immersed in water

If sulphuric acid be used in place of hydrochloric acid, the fragments of marble quickly become coated with a film of "insoluble" calcium sulphate which prevents further attack by the acid, and the evolution of gas practically ceases If the powdered calcium carbonate be suspended in water, sulphuric acid may be used. Marble sometimes contains sulphur compounds which lead to the formation of sulphur dioxide, the carbon dioxide will then have a distinct smell of burning sulphur By passing the gas through a wash-bottle containing a dilute sulphuric acid solution of potassium permanganate, most of the sulphur dioxide will be removed from the gas. The gas, prepared as indicated above, may also contain steam and a little hydrogen chloride, as well as air A fairly pure gas is

made by the action of dilute sulphuric acid on lumps of "fused" sodium carbonate In symbols

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2$$

Sodium sulphate is a by product of the reaction

Large-scale manufacture.—Some carbon dioxide for manufacturing operations is made by the action of sulphuric acid on magnesite, whereby magnesium sulphate is obtained as a by product It is also made as a by-product when limestone or magnesite is burned is special kilns In the latter case, the gas is purified by washing in towers, etc For some purposes, too, carbon dioxide mixed with atmospheric nitrogen is made by passing air over red-hot coke In the brewing industry, carbon dioxide is a by-product developed during the action of the yeast plant on sugar, or materials containing sugar This gas is then washed and pumped into steel cylinders to be afterwards made into mineral waters.

Fermentation.—The formation of carbon dioxide during the process of fermentation is very curious The fact can be illustrated by the following experiment Shake 50 c c of treacle with 400 c c of water in a litre flask, *A*, Fig 227, and add a few c c of yeast Connect the flask with a glass delivery tube, *B*, in communication with an empty wash-bottle, *C*, and another wash bottle, *D*, containing clear lime water The liquid in the flask, if kept warm, soon begins to bubble and froth—ferment The whole apparatus is left on one side until the next lesson The lime water will then be quite turbid, and the contents of *D* may be tested for calcium carbonate as indicated below The yeast plant during its growth decomposes the sugar—$C_6H_{12}O_6$—solution forming carbon dioxide and ethyl alcohol—C_2H_5OH The reaction, in symbols, is usually represented: $C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$ The alcohol remaining in the flask *A* can be partially separated by fractional distillation The last traces of water are removed from the distillate, boiling at about 80°, by distillation from freshly ignited lime, or recently fused potassium carbonate Ethyl alcohol, when pure, boils at 78 4° (atmospheric pressure)

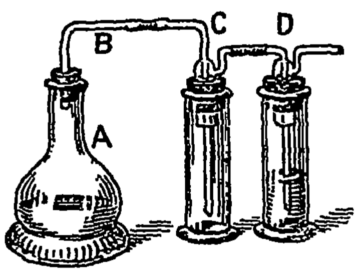


FIG 227.—The Fermentation of Sugar

The "raising of bread" depends upon the expansion of bubbles of carbon dioxide by heat The carbon dioxide is generated by the action of yeast on sugar or starch, or by the action of sodium bicarbonate ("baking soda") and a substance of acid reaction—tartaric acid, acid potassium tartrate (cream of tartar), etc The formation of carbon dioxide during this reaction is shown by examining the gas developed when a mixture of cream of tartar and baking soda is moistened with water

§ 2 The Properties of Carbon Dioxide

The gas is invisible, when breathed through the *nostrils*, it gives a tingling sensation, and it has an acid taste [1] If a jar of the gas be turned

[1] The student should never smell or taste substances indiscriminately—smelling hydrogen cyanide might prove fatal, and the tasting of many substances would be equally disastrous

upside down for a minute, the heavy gas falls out and air takes its place. The gas is therefore heavier than air, and, as indicated above, it extinguishes the flame of burning bodies. These properties—the invisibility of the gas, its heaviness compared with air, and its property of quenching flame—enable many pleasing and attractive experiments to be arranged, and limited only by the ingenuity and skill of the experimenter.

Thus (1) a long cardboard gutter leading into a glass trough in which a number of candles are burning can be arranged. The invisible gas, carbon dioxide, can then be poured from a large beaker down the gutter, when the candles will be extinguished just as if water had been poured down the gutter.

(2) A cylinder can be arranged with candles at different levels; the gas, when led into the cylinder, extinguishes the candles one by one as the gas rises in the jar.

(3) A wheel of stiff cardboard can be mounted upon two corks on a knitting needle journalled into a wooden standard; paper "buckets" can be attached to the periphery of the disc by joining the edges of the paper so as to form a hollow cone. When carbon dioxide is poured into the buckets, the wheel will rotate, if properly balanced, as if it were a "water wheel," moved by a stream of water.

(4) A cardboard box, or a light glass vessel can be counterpoised on a balance; the beam will be depressed when carbon dioxide is poured into the box, showing that the carbon dioxide is heavier than the air displaced.

(5) Soap bubbles blown with air can be floated on the carbon dioxide in a large dish.

(6) Petroleum burning in a shallow dish can be extinguished by pouring the gas over the dish; and a beaker of the gas poured over a lighted candle will quench the flame.

(7) Carbon dioxide can be ladled from a large cylinder by a small beaker tied on to a string. The action is analogous with the method of emptying a well of water by means of a bucket and rope. Finally, a candle will burn in the cylinder, showing that the carbon dioxide has been removed. The beakers of carbon dioxide can be emptied into another cylinder and the presence of carbon dioxide demonstrated in the usual way.

Carbon dioxide is an active agent in many portable fire extinguishers. Some contain sodium carbonate and sulphuric acid or alum solution so arranged that they can be mixed and the gases generated under pressure when desired. The stream of carbon dioxide forced on to the burning object might prevent a serious conflagration. In "chemical fire engines" the pressure of the gas itself is utilized to force a stream of water on to the burning body.

Action on animals.—A mouse placed in a jar of the gas will be suffocated in a very short time. Carbon dioxide is not particularly poisonous. Its harmful effects are mainly due to suffocation (absence of oxygen). Small increases in the amount of carbon dioxide in air—say 2 or 3 per cent.—do no perceptible harm; 5–6 per cent. induces a rise of pulse and marked panting; 10 per cent., violent panting; above this the gas exerts a narcotic effect, and with 25 per cent. death will occur in a few hours; air with 50 per cent. carbon dioxide can be breathed a short time without fatal results.

Solutions in water.—The solubility of carbon dioxide in water will be discussed later. Water dissolves about $1\frac{3}{4}$ times its volume of the gas at 0° and 760 mm. pressure; and about its own volume at 15°, 760 mm. In the manufacture of "soda water" the gas is dissolved by the water under great pressure—60–150 lbs. per square inch. The solution effervesces and froths when the pressure is withdrawn, owing to the escape of the carbon dioxide. Liquids bottled during fermentation—beer, champagne, kumiss, etc.—effervesce for the same reason. The same remarks apply to many

mineral waters, e g the water of the Geyser Spring (Saratoga), at Niederselters (Hesse-Nassau), Seidlitz (Bavaria), etc , p 149 Selters water is, in England, called "Seltzer water" Soda water, i e saturated with carbon dioxide, in the stomach acts as an aperient Stale beverages are sometimes "revived" by saturating them with carbon dioxide under pressure

Action of heat—Carbon dioxide is fairly stable at high temperatures. When heated under atmospheric pressure, at 1300°, only 0 004 per cent. is decomposed, at 1400°, 0 14 per cent, and at 1478°, 0 32 per cent The action is a reversal of the oxidation process $2CO_2 \rightleftharpoons 2CO + O_2$ So far as we can tell, two reactions are going on simultaneously when the rate at which the carbon dioxide is decomposed is equal to the rate at which the carbon monoxide is oxidized, the two reactions are balanced and the system is in equilibrium. Raising the temperature above 1300° augments the velocity of the process of decomposition

Action of metals—potassium, calcium, etc—If the gas be heated in contact with metallic potassium, sodium, calcium, or magnesium, the metals are oxidized, and the carbon of the gas separates in a solid condition Pass carbon dioxide from a suitable apparatus, *A* Fig 228, through a washing bottle, *B*, containing sulphuric acid, and then into a bulb of hard glass, *C*, containing a few shavings of metallic magnesium, potassium, or calcium When all the air has been expelled from the apparatus, the bulb is heated The carbon dioxide is decomposed vigorously, forming black carbon, and calcium carbonate $CO_2 + 2Ca \rightarrow 2CaO + C$, and $CaO + CO_2 = CaCO_3$ Metals like iron and zinc give carbon monoxide instead of carbon when heated with carbon dioxide $CO_2 + Zn \rightleftharpoons ZnO + CO$

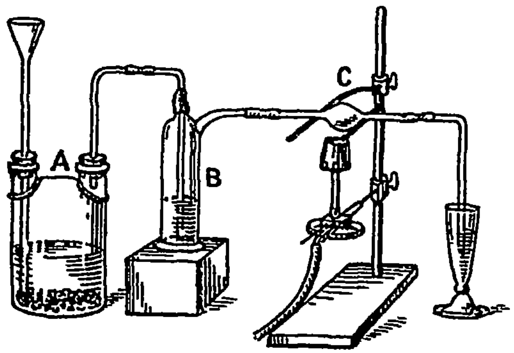


FIG 228—The Action of Metals on Carbon Dioxide

If a rapid stream of carbon dioxide be passed through pure water in which rods of amalgamated zinc are immersed, a little of the carbon dioxide is reduced to formaldehyde, H CO H, thus $CO_2 + 2H_2 = H_2O + H.CO H$ The yield is increased if a trace of ammonia be present

§ 3 Carbon Dioxide—Occurrence and History

Occurrence—Atmospheric air contains about 0 03 per cent of its volume of carbon dioxide, and on account of the occurrence of this gas in air, T Bergmann (1774) called it "acid of air" It issues from the ground in many places both as a gas and in aqueous solution (mineral water) J B Boussingault (1844) estimated that Cotopaxi emitted more carbon dioxide per annum than was generated by life and combustion in a city like Paris Owing to the fact that carbon dioxide is nearly one and a half times as heavy as air, this gas is inclined to collect as a gas in old deep wells,

in valleys, and in depressions in the ground near lime kilns, and in certain neighbourhoods where carbon dioxide is evolved from volcanoes and fissures in the ground—*e g* the Valley of Death (Lake of Laach, Java), the Grotta del Cane (Pozzuoli, Naples), etc The student must here distinguish between the *flow* of a heavy gas like carbon dioxide to the lowest possible level, and *diffusion* which leads to the dissipation of the gas into the atmosphere If the supply of gas were not kept up, the gas which collects in the low levels would gradually be diffused through the atmosphere Tremendous deposits of calcium and magnesium carbonates—chalk, limestone, dolomite—as well as smaller deposits of other carbonates, occur in various parts of the world.

History —Carbon dioxide has been known for a long time, but the early writers confused it with "air" J B van Helmont (p 10) called it *gas sylvestre*[1] to distinguish it from common air He prepared it by the action of acids on alkalies and calcareous substances, he showed that it was formed during the combustion of charcoal, during the fermentation and the decay of organic matter, and he recognized it in the "mineral water" at Spa (Belgium), in the Grotta del Cane (Naples), and other localities Van Helmont also knew that the gas extinguished flame, and suffocated animals. Van Helmont, however, confused it with other gases which do not support combustion J Black (1755), however, proved the gas to be a peculiar constituent of carbonated alkalies, being "fixed" there in the solid state Hence Black called the gas *fixed air*, and T Bergman (1774), *aerial acid* The chemical nature of carbon dioxide was clearly explained by Lavoisier, who showed it to be an oxide of carbon

§ 4 Liquid and Solid Carbon Dioxide.

Faraday liquefied carbon dioxide in 1823 by means of his sealed tube arrangement indicated in Fig 100, and liquid carbon dioxide is now manufactured as a commercial article by pumping the gas into steel cylinders (bombs) by powerful compression pumps The gas from, say, the fermenting vats of a brewery (p 654) is washed, purified, and pumped into the bombs for "aerated water" manufacture, etc

Properties of liquid carbon dioxide —At $-5°$, carbon dioxide requires a pressure of 30 8 atmospheres for liquefaction, at $+5°$, 40 4 atms, and at $+15°$, 52 1 atms, and over $32°$ it cannot be liquefied by any known pressure Liquid carbon dioxide is a colourless mobile liquid It floats on water without mixing with it It boils at $-78\ 2°$ at atmospheric pressure Carbon dioxide is used as a refrigerating agent on board ships where the use of ammonia for the same purpose is objectionable on account of the smell from slight leakages According to a Board of Trade regulation, if ammonia refrigeration machines are used on board ship, the compression apparatus must have a special compartment

Solidification of liquid carbon dioxide —If liquid carbon dioxide be allowed to escape into the air from the nozzle of the bomb, the absorption of heat which attends the rapid evaporation causes a *portion* of the liquid to solidify The solid is collected by tying a small canvas bag over the nozzle and inverting the bomb By opening the nozzle for a few minutes,

[1] The term "sylvestre" possibly refers to the supposed impossibility of condensing it, or it is to be taken literally as the "wild gas" which dwells in out of the-way places, or having prepared the gas from charcoal, he thought of the *sylvan* surroundings of the charcoal burners

quite a lot of solid carbon dioxide can be collected. The solid can be shaken from the bag into a cardboard box for examination

✓ **Properties of solid carbon dioxide**—Solid carbon dioxide is a soft white snow like substance—"carbonic acid snow" It evaporates in air without melting, but under a pressure of 5 atms it can be melted to a liquid It can be handled safely provided no pressure is applied. The effect of pressure is to break the film of gas between the solid and the warm hand and cause a severe burn, or rather, a blister, resembling the blister produced by a burn A horn spoon can be used for handling the material A piece of the solid, if placed inside an empty beaker, will evaporate sufficiently in a few minutes to fill the beaker with carbon dioxide gas to which the usual tests can be applied Place some of the solid in a soda water bottle and close the bottle with a rubber stopper In a short time, the gas evolved will generate sufficient pressure to blow the stopper out of the bottle A small beaker can be placed on a few drops of water on a wooden block. Some solid carbon dioxide is placed in the beaker In a few minutes, the beaker will be frozen to the wood

Carbon dioxide "snow" dissolves in ether, and as the ether evaporates, a temperature approaching −110° can be obtained in air, and −140° under reduced pressure The solution is a good conductor for heat, and serves as an excellent freezing mixture A great many gases can be liquefied by passing them through tubes immersed in this mixture Several interesting experiments can be made to illustrate the change in the properties of metals, etc, at low temperatures by means of solid carbon dioxide, or its solution in ether Mercury freezes to a malleable solid resembling metallic lead

The freezing of mercury is conveniently demonstrated as follows A circular groove—1 cm deep, 1 cm wide, and 7 cm diameter on the inside of the ring—turned in a block of wood is filled about 7 mm deep with dry mercury Put the wooden mould in a large porcelain dish, fill the space around the mould with cotton wool, cover the mercury with a 7 mm layer of solid carbon dioxide or a mixture of carbon dioxide and ether The mercury will be frozen in a few minutes Invert the mould, and the mercury ring falls out Lift the mercury ring rapidly with a glass hook, and lower it into a cylinder of water as illustrated in Fig 229 The ring is at once covered with a layer of ice The mercury melts before the ice, and leaves a ring of ice on the hook while it runs to the bottom of the cylinder, the ice itself melts in a few minutes

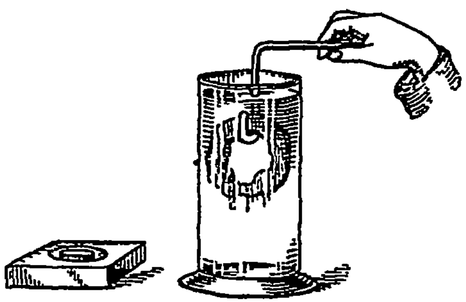


FIG 229—Freezing Mercury—F G Benedict

§ 5 The Composition of Carbon Dioxide

1 **Composition by weight**—This has been established by the work of Dumas, Stas, Erdmann and Marchand, Roscoe, Friedel, etc A weighed amount of carbon—diamond, graphite, etc—is burnt at a red heat in a platinum boat, placed in a porcelain tube, *C*, Fig 154 The tube also contains a layer of hot copper oxide A stream of oxygen purified from carbon

dioxide by passing through wash-bottles, *B*, containing potassium hydroxide and sulphuric acid, is led over the hot carbon The resulting gas, on passing through the hot copper oxide, is all oxidized to carbon dioxide The carbon dioxide is absorbed in weighed potash bulbs, *D*, and in a U-tube *E* containing soda lime in one leg, and calcium chloride in the other The platinum boat containing the carbon is weighed before and after the experiment so that due allowance can be made for any ash present in the original sample of carbon The following numbers are selected from the original list of experiments

1 0000 gram of sugar charcoal required	2 6662 grams oxygen
1 0000 gram of graphite required	2 6659 grams oxygen
1 0000 gram of diamond required	2 6662 grams oxygen

Hence the combining ratios of carbon and oxygen in carbon dioxide are 8 grams of oxygen per 3 001 grams of carbon, or 11 001 grams of carbon dioxide, or, 32 grams of oxygen require 12 004 grams of carbon to form 44 004 grams of carbon dioxide The numbers obtained by different experimenters range from 11 99 to 12 00, and consequently 12 is taken to be the best representative value for the atomic weight of carbon (see p 62) This experiment not only shows the relation between the weights of carbon and oxygen in carbon dioxide, but it also shows that the same relation obtains, within the limits of experimental error, whether the carbon be diamond, graphite, or charcoal

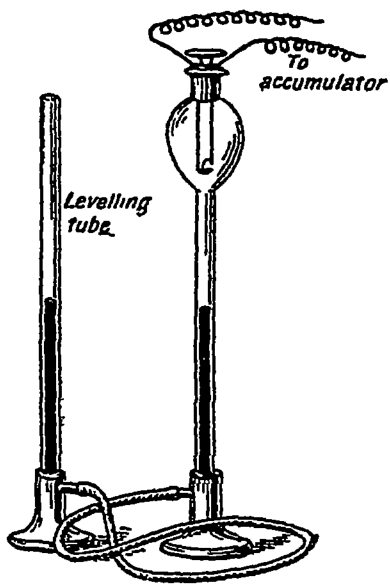


FIG 230 —Volume Synthesis of Carbon Dioxide

2 Relative density of carbon dioxide —This constant, determined by weighing an empty globe, and then the globe filled with gas, shows that if the density of oxygen is 32, that of carbon dioxide is 44 26 Hence the molecular weight of carbon dioxide is nearly 44 26 This is only possible if 12 parts of carbon are combined with 32 parts of oxygen by weight With the atomic weight of oxygen 16, and carbon 12 003, it follows that the formula of carbon dioxide must be CO_2

3 Composition by volume —The volume of a solid is negligibly small in comparison with the volume of the same substance in the gaseous state Hence, if solid carbon be burnt in oxygen, Avogadro's hypothesis would lead to the inference that one volume of oxygen will form an equal volume of carbon dioxide·

$$\underset{\text{(Solid)}}{C} + \underset{2\text{ vols}}{O_2} = \underset{2\text{ vols}}{CO_2}$$

This is best illustrated experimentally by means of the following modification of Hofmann's eudiometer charged with mercury, Fig 230 The bulb of the right tube, Fig 230, is charged with oxygen, and the stopper which carries a bone ash crucible containing a chip of charcoal, is lowered

into the position illustrated in the diagram A slip of gummed paper is placed on the right tube indicating the position of the mercury when that liquid is at the same level in both tubes The platinum wires are connected with an accumulator or battery The small loop of platinum wire in contact with the carbon is thus heated red hot. This ignites the carbon which burns to carbon dioxide The heat of the combustion expands the gas, but in a short time, when the apparatus has cooled, the level of the mercury is the same as before the experiment [1] Hence carbon dioxide contains the equivalent of its own volume of oxygen

§ 6 Carbonic Acid and the Carbonates and Bicarbonates

Carbonic acid—Neither liquid nor dry gaseous carbon dioxide affects dry blue litmus paper, but if the paper be moistened, the litmus is coloured red, and the blue colour is restored when the paper is dried There is little doubt that a small part of the carbon dioxide which dissolves in the water combines with the water to form carbonic acid The aqueous solution of the gas turns blue litmus red [2] Since carbon dioxide combines with water to form an acid, it is also called **carbonic anhydride** The acid is probably $O{=}C(OH)_2$ or H_2CO_3 The acid is unstable, and has not been isolated The acid decomposes at ordinary temperatures when the solutions are exposed to the air, and the carbon dioxide escapes It is probable that we have to deal with the reversible reaction $H_2O + CO_2 \rightleftharpoons H_2CO_3$ Only a very small quantity of the acid is formed as is evident from the low solubility of the gas in water The system is in equilibrium when but a small proportion of the dissolved gas has produced H_2CO_3 If a base be present, it will react with the carbonic acid and form a carbonate More H_2O and CO_2 unite, and the resulting H_2CO_3 is removed by the base as fast as it is formed, until all the carbon dioxide in solution has been converted into carbonate

Orthocarbonic acid corresponding with $C(OH)_4$, or H_4CO_4 is not known, although some **orthocarbonates**, *e.g* ethyl orthocarbonate, $C(OC_2H_5)_4$, are familiar to the student of organic chemistry The ordinary "carbonates," now to be considered, are really **metacarbonates** derived from **metacarbonic acid**, $CO(OH)_2$ The so called **formic acid** may be regarded as a derivative of metacarbonic acid made by replacing one hydroxyl group by hydrogen

$$\begin{array}{ccc} \begin{matrix}HO\\HO\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\OH\end{matrix} & \qquad \begin{matrix}HO\\HO\end{matrix}\!>\!C{=}O & \qquad \begin{matrix}H\\HO\end{matrix}\!>\!C{=}O \\ \text{Orthocarbonic acid} & \qquad \text{Metacarbonic acid} & \qquad \text{Formic acid} \end{array}$$

Alkali carbonates and bicarbonates—As just indicated, the hydroxide $C(OH)_4$ is unknown The first dehydration product $O{=}C(OH)_2$ is metacarbonic acid, or simply carbonic acid Carbonates contain "CO_3" as a dyad radicle There are two possible alkali carbonates—normal and acid

$$\begin{array}{ccc} \begin{matrix}HO\\HO\end{matrix}\!>\!C{=}O & \qquad \begin{matrix}NaO\\HO\end{matrix}\!>\!C{=}O & \qquad \begin{matrix}NaO\\NaO\end{matrix}\!>\!C{=}O \\ \text{Carbonic acid} & \qquad \text{Acid sodium carbonate} & \qquad \text{Normal sodium carbonate} \end{array}$$

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[1] The necessary adjustment of the levelling tube during and after the combustion will be obvious

[2] If the water contains traces of bicarbonates—*e g* hard water—the litmus will be coloured "wine red" or "claret red"

The normal salt is formed during the first action of carbon dioxide on sodium hydroxide $2NaOH + CO_2 = Na_2CO_3 + H_2O$ Sodium bicarbonate or sodium hydrogen carbonate or acid sodium carbonate, $NaHCO_3$ is formed when an aqueous solution of the normal carbonate is treated with an excess of carbon dioxide $Na_2CO_3 + H_2O + CO_2 \rightleftharpoons 2NaHCO_3$ Here the radicle "HCO_3" acts as a monad.

The great avidity of sodium hydroxide for carbon dioxide may be illustrated by several ingenious experiments. One of the simplest is to collect a cylinder of carbon dioxide over mercury and then pipette some sodium hydroxide solution under the edge of the cylinder The sodium hydroxide rises to the top of the mercury, absorbs the gas, and the mercury rises in the cylinder accordingly Potassium hydroxide is a better absorbent for carbon dioxide than the sodium hydroxide, because when a gas charged with carbon dioxide is bubbled through a wash-bottle the exit may become choked with solid sodium bicarbonate, because the sodium bicarbonate is less soluble in water than potassium bicarbonate (p 662)

Solutions of potassium hydroxide are largely employed in analytical work as an absorbent for carbon dioxide If air charged with carbon dioxide be drawn through a solution of sodium hydroxide in a weighed wash-bottle, the increase in weight represents the weight of carbon dioxide absorbed by the hydroxide If the volume of the air be known, the amount of carbon dioxide in that volume of air follows at once Similarly in gas analysis, the amount of carbon dioxide is determined from the contraction in volume which a given volume of the gas suffers after the gas has been in contact with sodium hydroxide

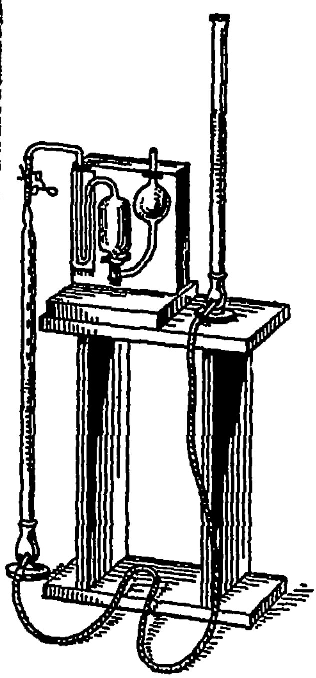


Fig 231 —Analysis of Gases containing Carbon Dioxide

The determination of carbon dioxide in a gas —Hempel's burette, previously described, is fitted with a pipette like that shown in Fig 231 charged with a 33 per cent solution of potassium hydroxide in water The cylindrical part is filled with short cylindrical rolls of iron wire gauze 1 to 2 mm mesh The rolls are from 1 to 2 cm long, and about 5 mm thick The iron does not oxidize during a determination because it is protected by the adherent solution The level of the potash solution is adjusted to a fixed point on the capillary tube, and connected with the gas burette by thick rubber tubing in the usual way The measured volume of gas is driven from the burette to the pipette, and after standing for about a minute, the gas is returned to the burette One absorption usually suffices to remove the carbon dioxide from a gas The difference in the level of the burette before and after the absorption indicates the amount of carbon dioxide absorbed by the *solution* in the pipette

Normal carbonates give an immediate precipitate with magnesium sulphate; bicarbonates give a precipitate on boiling With mercuric

chloride, normal carbonates give a reddish precipitate, bicarbonates give no precipitate

Sodium carbonate crystallizes from water as a decahydrate $Na_2CO_3.10H_2O$, in monoclinic prisms, potassium carbonate crystallizes as the anhydrous salt, K_2CO_3. The former is efflorescent, the latter deliquescent. The solubilities of the carbonates and bicarbonates of lithium, sodium, and potassium—grams of salt per 100 c.c. of water at 20°—are as follows

	Lithium	Sodium	Potassium
Carbonate (R_2CO_3)	1.33	21.4	112.0
Acid carbonate ($RHCO_3$)	5.5	9.84	26.9

Sodium and potassium bicarbonates are thus less soluble than the normal salts. Lithium bicarbonate, like the bicarbonates of the alkaline earths, is more soluble than the normal carbonate. The solubility of sodium carbonate decreases with rise of temperature owing to the formation of lower hydrates. Thus between 30° and 50°, rhombic prisms of the heptahydrate, $Na_2CO_3.7H_2O$, crystallize from the solution. Crystalline sodium carbonate, $Na_2CO_3.10H_2O$, melts at 60°, and on prolonged heating at this temperature, crystals of the dihydrate, $Na_2CO_3.2H_2O$, are deposited. These form the monohydrate, $Na_2CO_3.H_2O$, if dried over sulphuric acid, all the water is lost at 100°. Hot concentrated aqueous solutions of potassium carbonate deposit crystals of the trihydrate, $K_2CO_3.3H_2O$, these crystals, at 100°, lose two molecules of water forming the monohydrate $K_2CO_3.H_2O$. The latter become anhydrous at 130°. Anhydrous sodium carbonate melts at about 850°, and potassium carbonate at 880°, mixtures of the two melt at lower temperatures. The eutectic mixture $K_2CO_3 + Na_2CO_3$—the so called *fusion mixture*—melts about 690°

The bicarbonates are transformed into the normal carbonates on calcination. Sodium bicarbonate is one ingredient of baking powder and it is hence called "baking or cooking soda". When mixed with acid sodium tartrate (cream of tartar), which has a feeble acid reaction carbon dioxide is evolved; this puffs up the dough, hence the term "*salæratus*" is sometimes applied to this salt—the salt which aerates from the Latin *sal* salt *aer* air or gas. Effervescent powders like "Seidlitz powder" are mixtures of sodium bicarbonate with tartaric acid acid sodium tartrate or some similar acid or salt. The mixture reacts when moistened, liberating carbon dioxide. Sodium bicarbonate is used in medicine for neutralizing the acidity of the stomach

Sodium carbonate and bicarbonate are hydrolyzed in aqueous solution $Na_2CO_3 + H_2O \rightleftharpoons NaOH + NaHCO_3$, and the latter $NaHCO_3 + H_2O \rightleftharpoons NaOH + H_2CO_3$, and the carbonic acid dissociates as indicated above $H_2CO_3 \rightleftharpoons H_2O + CO_2$. The condition of equilibrium is therefore somewhat complex. As a result of the hydrolysis, aqueous solutions are somewhat alkaline, and lose carbon dioxide when warmed

Hydrolysis of sodium carbonate.—Reference might now be made to the discussion on the hydrolysis of zinc sulphate, and similar principles can be applied to the hydrolysis of sodium carbonate. Sodium carbonate in dilute aqueous solutions is completely ionized $Na_2CO_3 \rightleftharpoons 2Na^{\cdot} + CO_3''$. Water, as we have seen, is but slightly ionized $H_2O \rightleftharpoons H^{\cdot} + OH'$. The carbonate ions, CO_3'', react with the $H^{\cdot}$ ions of water to form feebly ionized carbonic acid, H_2CO_3, more water molecules ionize so as to maintain the equilibrium value $H_2O \rightleftharpoons H^{\cdot} + OH'$, and the process continues

until the concentration of the carbonic acid molecules has attained the equilibrium value $H_2CO_3 = 2H + CO_3''$ When that occurs, a considerable proportion of the H ions from the water have been "withdrawn" from the solution to form carbonic acid molecules, and an excess of OH' ions remain in solution, "paired," so to speak, with the Na ions of sodium hydroxide The scheme may be represented

$$\begin{array}{ccccc} Na_2CO_3 & \rightleftharpoons & 2Na & + & CO_3'' \\ & & + & & + \\ 2H_2O & \rightleftharpoons & 2OH' & + & 2H \\ & & \updownarrows & & \updownarrows \\ & & 2NaOH & & H_2CO_3 \end{array}$$

An aqueous solution of sodium carbonate behaves in many ways like a solution of sodium hydroxide—turns red litmus blue, etc —and the ionic hypothesis thus shows how this action can be referred to the presence of an excess of OH' ions If an hydrochloric acid solution be added to a solution of sodium carbonate, the H ions of the acid unite directly with the OH' ions in the solution to form water, and if just sufficient HCl be added to remove the OH' ions, the solution will contain nothing more than Na and Cl' ions such as would be obtained by dissolving sodium chloride in water The CO_3'' ions of carbonic acid, and the Cl' ions of the hydrochloric acid, are competing for the Na ions, but carbonic acid is very feeble in comparison with hydrochloric acid. and carbon dioxide formed by the *dissociation*, not ionization, of the carbonic acid is volatile under the conditions of the experiment and escapes from the solution.

Calcium carbonate and bicarbonate—Calcium carbonate has been previously studied, p 329 Calcium carbonate is precipitated when a soluble carbonate, say, sodium carbonate, is added to a soluble calcium salt $CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$. Calcium carbonate is also precipitated when a current of carbon dioxide is passed into lime-water $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$ Hence clear lime-water is rendered turbid by contact with carbon dioxide This is a common test for carbon dioxide Baryta water is still more sensitive If an excess of carbon dioxide be passed through the solution, some of the calcium carbonate redissolves, and if the solution be not too concentrated, the turbidity may be clarified This is due to the formation of a soluble calcium bicarbonate, $Ca(HCO_3)_2$—acid calcium carbonate or calcium hydrogen carbonate $CaCO_3 + H_2O + CO_2 \rightleftharpoons CaH_2(CO_3)_2$. The relations of these carbonates will appear from the graphic formulæ

$$\begin{matrix} HO \\ HO \end{matrix}\!>C{=}O \qquad O{=}C<\begin{matrix} OH \\ O\text{—}Ca\text{—}O \end{matrix}\begin{matrix} HO \\ {} \end{matrix}\!>C{=}O \qquad Ca<\begin{matrix} O \\ O \end{matrix}>C{=}O$$

Carbonic acid — Acid calcium carbonate — Normal calcium carbonate

The acid carbonate is not very stable and it cannot be isolated by concentrating the aqueous solution, since it decomposes on exposure to the air owing to the escape of carbon dioxide and the precipitation of calcium carbonate, the solution likewise decomposes when boiled $Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2$, and when treated with lime water, the two lime compounds react, precipitating calcium carbonate:

$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$ The bicarbonates of the alkaline earths have been isolated by mixing solutions of ammonium or potassium bicarbonate with the corresponding chloride all cooled to 0° With calcium chloride, potassium bicarbonate furnishes a white crystalline precipitate with the ultimate composition $Ca(HCO_3)_2$

The carbonates are not quite insoluble in water, 100 c c of water at 8 7°–8 8°, dissolve 0 0016 gram of barium carbonate, 0 10 gram of calcium carbonate, and 0 008 gram of strontium carbonate. Pure calcium carbonate imparts an alkaline reaction to water, probably owing to hydrolysis $2CaCO_3 + 2H_2O \rightleftharpoons Ca(HCO_3)_2 + Ca(OH)_2$ The precipitation of the carbonates of the alkaline earths by ammonium carbonate is a reversible reaction $CaCl_2 + (NH_4)_2CO_3 \rightleftharpoons CaCO_3 + 2NH_4Cl$ Hence an excess of ammonium carbonate favours more complete precipitation, and the presence of ammonium chloride leads to a resolution of the precipitate Magnesium carbonate is hydrolyzed by much water, and a basic carbonate is precipitated A basic magnesium carbonate is precipitated by adding sodium carbonate to the solution of a magnesium salt The composition of the precipitate depends upon the temperature, concentration, etc, of the solutions at the time of precipitation "Magnesia alba" of commerce has approximately the composition $(3MgCO_3 Mg(OH)_2)$ Some consider that the normal carbonate is first formed and immediately hydrolyzed by the water The insolubility of magnesium hydroxide leads to its joint precipitation with the carbonate

The carbonates of zinc, mercury, lead, and copper, like magnesium, are readily hydrolyzed, and produce basic carbonates In the case of solutions of salts of iron and aluminium, alkaline carbonates precipitate the hydroxides It is supposed that the hydrolysis of the carbonate is here complete Normal zinc carbonate occurs native as *calamine*, $ZnCO_3$, and the normal carbonate is precipitated from soluble zinc salts by potassium hydrogen carbonate The excess of carbon dioxide is used to prevent hydrolysis. Cadmium does not form a normal carbonate

§ 7 Lead Carbonates—White Lead

Normal lead carbonate, $PbCO_3$, is precipitated when an alkaline bicarbonate is added to a soluble lead salt as in the case of zinc, a basic carbonate is precipitated if normal alkaline carbonate is used. Native lead carbonate, $PbCO_3$, is called *cerussite* It is isomorphous with aragonite, $CaCO_3$, and witherite, $BaCO_3$ Barium does not form a basic carbonate, and it does not lose carbon dioxide so readily as lead carbonate The latter decomposes at about 200° into lead monoxide and carbon dioxide, and at the same temperature it is readily reduced to the metal by carbon monoxide The most important basic lead carbonate has approximately the composition $2PbCO_3.Pb(OH)_2$, it is known as "white lead." White lead is largely employed as a pigment, and in the manufacture of pottery glazes It is made by a number of different processes

Stack or Dutch process of manufacturing white lead—The old so called Dutch vinegar process—said to have been "old" in 1662—is supposed to give a better product than any other process A layer of 3 per cent. acetic acid is placed in the bottom of a large number of earthenware pots A roll of thin metallic lead is placed on a shoulder in the pot above

the acetic acid The pots are placed upon a bed of spent tan bark from the leather tanning yards[1] The layer of pots is covered with boards A layer of tan bark is placed on the boards, and then a second row of pots similarly charged. A chamber is nearly filled with pots in this manner There are many variations in the methods of placing the pots, etc For instance, in Cookson's works, "straps" of "blue" lead are laid over rows of plain pots as illustrated in Fig 232 The pots are charged with acid as before, and rested upon tan bark, and boards, resting on supports *A*, separate one layer from another The lead acid pots and tan bark are thus confined in a series of little chambers In about twelve weeks, most of the lead will have been transformed into compact masses of white lead The stacks are then unloaded and the white lead is crushed in a mill, any lumps of unchanged lead are removed The white lead is then ground up with water, passed into settling tanks, and finally dried.

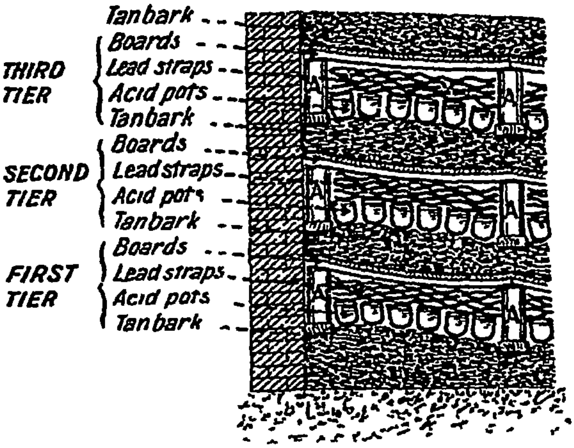


FIG 232 —Section through Lower Corner of a White lead Stack (Diagrammatic)

The reactions which occur in each chamber are probably as follows The heat developed by the decomposition of the tan bark volatilizes the acetic acid which forms a basic lead acetate For convenience in writing the equations, put $\bar{A}$, for the radicle of acetic acid and the acetates, *viz* $C_2H_3O_2$ The reaction just mentioned is symbolized $2H\bar{A} + 2Pb + O_2 = Pb\bar{A}_2 \, Pb(OH)_2$ The basic acetate so formed is decomposed by the carbon dioxide evolved during the decomposition of the tan bark A mixture of normal lead acetate and basic lead carbonate is formed $3[Pb\bar{A}_2 \, Pb(OH)_2] + 2CO_2 = 3Pb\bar{A}_2 + 2PbCO_3 \, Pb(OH)_2 + 2H_2O$ The lead acetate in the presence of air and moisture reacts with more lead, forming more of the basic lead acetate $2Pb\bar{A}_2 + 2Pb + O_2 + 2H_2O = 2[Pb\bar{A}_2.Pb(OH)_2]$ A small amount of lead acetate will thus serve for the manufacture of an indefinite amount of white lead

The chamber corrosion process —In this process straps of "blue" lead—about six inches wide and over a yard long—are hung on a series of horizontal bars arranged in tiers Air, acetic acid vapour, steam, and carbon dioxide are admitted into the chamber maintained at the most favourable temperature In about forty five days the chambers are "drawn," and the corroded lead is washed, etc, as before

Many other more rapid processes have been proposed, *e g* electrolytic processes. In Thénard's process carbon dioxide is passed into a solution of basic lead acetate made by boiling litharge with lead acetate The rapid processes may furnish a product of equal chemical purity with the stack processes, but the consumer frequently prefers white lead made by the

[1] Wet hay or dung has also been used

older and more expensive stack process The difference between white lead made by the different processes is not a question of chemical composition The covering power of white lead made by the stack and corrosion processes is usually greater than that prepared by other processes As a result less white lead is needed to impart to a given surface a given degree of opacity White lead is liable to turn yellow or brown when exposed to the air of towns owing to the formation of lead sulphide, PbS For some purposes, therefore, white paints made from zinc oxide, lead sulphate, or barium sulphate are preferred in spite of their low covering power

§ 8 Hard and Soft Water

Water comes very near to the "universal solvent" (p 158) of the alchemists' dreams Natural water holds carbon dioxide in solution, and when such water comes in contact with magnesium and limestone rocks, some may be dissolved Water holding magnesium and calcium salts in solution is said to be hard The term is applied on account of the difficulty of obtaining a soap lather with such water Soap is a compound of sodium with a fatty acid The soap is decomposed by magnesium or calcium salts The fatty acid unites with the latter to form an insoluble curdy precipitate. This action continues until all the lime and magnesian salts have been precipitated Any further addition of soap at once produces a lather, and the soap can then be used as a cleansing agent If a solution of soap of definite strength and a definite volume of water be employed, the hardness of a given sample of water can be represented in terms of the amount of soap required to produce a lather The hardness of water thus refers to the "soap destroying power" of the water and it is expressed in degrees *Each degree of hardness corresponds with one grain of calcium carbonate, or its equivalent in other calcium or magnesium salts per gallon of water.* Hardness is also expressed in parts of calcium carbonate, or its equivalent, per 100,000 parts of water Waters containing but small quantities of lime and magnesian salts lather freely with soap and they are accordingly called **soft waters** A water less than 5° hardness may be called "soft," and a water between 18° and 20° hardness is "moderately hard," and if over 30° hardness, "very hard" Very soft waters are liable to attack metals like lead, zinc, and iron

The process of removing lime salts from hard water is called **softening the water** In the case just cited, soap is the softening agent If the hardness of the water be due to the presence of acid carbonates of calcium or magnesium, mere boiling will soften the water because, as indicated above, the acid carbonates are then decomposed, and the normal carbonates are precipitated **In Clark's process for softening water** (1841) the necessary amount of milk of lime or lime water is added to convert all the acid carbonates of lime and magnesium into the normal carbonate We have here the curious paradox—"add lime to remove lime" The theory of the action has been previously discussed p 664

Hard water may be wholly or partially softened by boiling That part of the hardness so removed is termed **temporary hardness**, the degree of hardness which remains after prolonged boiling is called **permanent hardness** Temporary hardness is due to the presence of calcium and magnesium bicarbonates, permanent hardness is due to the presence

of calcium and magnesium chlorides or sulphates[1] After removing the temporary hardness, if present, by boiling or by Clark's lime process, the permanent hardness may be removed by the addition of sodium carbonate. The sodium carbonate precipitates the calcium and magnesium as insoluble carbonates. $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$. The water still contains sodium sulphate and sodium chloride, but the presence of a small quantity of these salts is not usually objectionable. Sodium carbonate will remove temporary as well as permanent hardness. The processes used for softening potable hard water may thus be summarized: (1) Distillation, (2) Boiling, (3) The addition of lime with or without soda ash or other chemicals. The former is usually too expensive.

The Report of the Rivers Pollution Commission classified unpolluted water as is shown in Table XLIX, which represents the average of a number of analyses of each type.

TABLE XLIX.—AVERAGE COMPOSITION OF UNPOLLUTED NATURAL WATERS.

Class of Water	Total solids	Organic carbon	Organic nitrogen	Ammonia	Nitrogen (nitrates and nitrites)	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Rain	2.95	0.070	0.015	0.029	0.003	0.042	0.822	0.4	0.5	0.9
Upland surface	9.67	0.322	0.032	0.002	0.009	0.042	1.130	1.5	4.3	5.8
Deep well	43.78	0.061	0.018	0.012	0.495	0.522	5.11	15.8	9.2	25.0
Spring	28.20	0.056	0.013	0.001	0.383	0.396	2.49	11.0	7.5	18.5

Boiler scale.—The "furring" of kettles, and the formation of "boiler scale," is due to the precipitation of calcium and magnesium salts. Boiler scale is a poor conductor of heat, and hence the efficiency of a boiler which has "scaled" is seriously impaired. The boiler scale and the metal have different rates of contraction and expansion by heat. If the water in the boiler gets low, and the metal overheated, the "scale" may separate from the metal. If cold water now runs into the boiler, the scale quickly cools, contracts, and cracks. Water pours through the cracks on to the hot metal, a large volume of steam is generated, and the sudden pressure may be great enough to burst the boiler. Hard water in steam boilers not only produces "boiler scale," but it may corrode the boiler shell, and cause "foaming" and "bumping." The corrosion and pitting of boilers is usually produced by soft waters from swampy districts which contain organic acids in solution, by water from mining districts containing mineral acids in solution (*e.g.* sulphuric acid from the oxidation of pyrites, *q.v.*), and by water containing magnesium or calcium chlorides and nitrates. A great many nostrums for preventing boiler scale and corrosion have been proposed. In some, the water is treated before it enters the boiler, in others, the water is softened in the boiler itself. Whatever

[1] There is a kind of "pseudo hardness" due to the insolubility of soap in water containing sodium chloride. The so called "marine soaps" are fairly satisfactory for such waters.

agents be used, they must be cheap, easily applied, yield no acid when used, and precipitate the salts which make the water hard in a flocculent powdery condition easily blown from the boiler.

Among the commoner agents are sodium or calcium hydroxide, and sodium carbonate discussed above, sodium aluminate, $NaAlO_2$, which acts as represented by the equation $2NaAlO_2 + Ca(HCO_3)_2 + 2H_2O = Na_2CO_3 + 2Al(OH)_3 + CaCO_3$ sodium fluoride which acts $2NaF + Ca(HCO_3)_2 = 2NaHCO_3 + CaF_2$, normal sodium phosphate, which acts $2Na_3PO_4 + 3CaSO_4 = 3Na_2SO_4 + Ca_3(PO_4)_2$, etc

Hard water in nature—Water highly charged with dissolved calcium bicarbonate may be dripping through the roof of a cave or subterranean cavern Some carbon dioxide escapes from the solution, and a certain amount of calcium carbonate is deposited Each drop adds its own little share of calcium carbonate The deposit grows—maybe on the roof, where it is called a stalactite, maybe on the floor, when it is called a stalagmite All depends upon the time occupied by each drop in gathering and dropping The stalagmite grows upwards from the ground, and the stalactite grows downwards, like an icicle, from the roof In time, the two

Fig 233—Stalactites and Stalagmites in the Yarrangobilly Caves, N S W[1]

may meet and form a pillar Fig 233 conveys but little idea of the beauty of some limestone caverns in which stalactites and stalagmites have been growing The photograph shows stalactites, stalagmites, and pillars which have no doubt been formed in this manner The San Filippo spring (Tuscany) is said to deposit "lime" at the rate of 12 inches a month, and the spring has formed a bed of limestone rock 250 feet thick, $1\frac{1}{4}$ miles long, and $\frac{1}{4}$ mile wide The building stone called *travertine* (Tiberstone) is probably a limestone deposited from a mineral spring The Colosseum and much of ancient and modern Rome were built with this stone

[1] Given me by the Agent General, N S W

§ 9 Alkali Manufacture

Before 1793, sodium carbonate was made from the ashes of seaweeds and potash carbonate from the ashes of land plants Several methods were known at that time for converting sea salt into sodium carbonate, *e g* K. W Scheele, about 1776, converted salt into soda by treating a solution of salt with lead oxide and passing carbon dioxide into the filtered solution When Napoleon closed the European ports to English and American ships the main sources of supply of sodium carbonate and potashes were cut off To ease the demand, Napoleon offered a prize of 100,000 francs for a process of manufacturing soda from common salt The prize was won by N Leblanc, 1794, who proposed a method of manufacture which has held its own for over 100 years, although it has had a serious rival in the ammonia soda or Solvay's process, and both processes have to compete against electrolytic processes Had it not been for the commercial value of the by-products of Leblanc's process, there can be little doubt that it would have been ousted long ago

Electrolytic processes —The electrolytic processes of manufacture depend upon the formation of sodium hydroxide during the electrolysis of aqueous solutions of sodium chloride The chlorine obtained as a by-product is used in the manufacture of bleaching powder The hydroxide is converted into sodium carbonate by treatment with carbon dioxide, which is obtained as a by-product in the fermentation industries, etc Everything is utilized so that the cost essentially depends upon the price of the current used

§ 10 N Leblanc's Black Ash Process.

In studying the principle of the Leblanc's process it will be convenient to take it in different stages

1 **Conversion of sodium chloride into sodium sulphate—salt-cake** —The first stage in the process is to convert the sodium chloride into sodium sulphate by the action of sulphuric acid The reaction has been previously discussed, p 440 The product of this reaction is sodium sulphate, also called salt cake

2 **The conversion of salt-cake into black ash** —The salt-cake is mixed with limestone and coal, and heated to a high temperature in a reverberatory furnace (black ash furnace), or in a furnace with a revolving cylinder so arranged that the hot gases from the furnace pass through the cylinder, Fig 234 The cylinder contains the mixture of salt-cake, limestone, and coke, and the slow revolution of the cylinder ensures the thorough mixing of the contents The sodium sulphate is reduced by the carbon $Na_2SO_4 + 2C = Na_2S + 2CO_2$ The resulting sodium sulphide reacts with the limestone, forming calcium sulphide and sodium carbonate $Na_2S + CaCO_3 = CaS + Na_2CO_3$ The initial and end stages of the reaction are symbolized $Na_2SO_4 + CaCO_3 + 2C = Na_2CO_3 + CaS + 2CO_2$ The contents of the cylinder are then discharged into iron *trucks*. The dark grey or brown porous mass so obtained is called *black ash* Black ash contains 40 to 45 per cent of sodium carbonate, 30 to 33 per cent of calcium sulphide, calcium oxide, 2 to 6 per cent;

calcium carbonate, 6 to 10 per cent, coke, 4 to 7 per cent, and smaller quantities of sodium sulphide, sodium chloride, iron oxide, etc

3 **Extraction of sodium carbonate from black ash**.—The black ash is rapidly lixiviated with warm water so that as little water as practicable will be used. The water passes through a series of tanks containing the pulverized ash. Fresh water passes through the tank containing the ash which is almost all extracted, and the water, almost saturated, passes through the black ash fresh from the furnace. The tank liquid is allowed to settle, and then concentrated by evaporation in shallow pans heated by the waste heat from the black ash furnace. The product of the evaporation is then calcined—it is called crude soda ash. The latter is further purified by exposing it to a current of hot air in order to oxidize the sulphides to sulphates. The sulphides impart a slight yellow tinge to

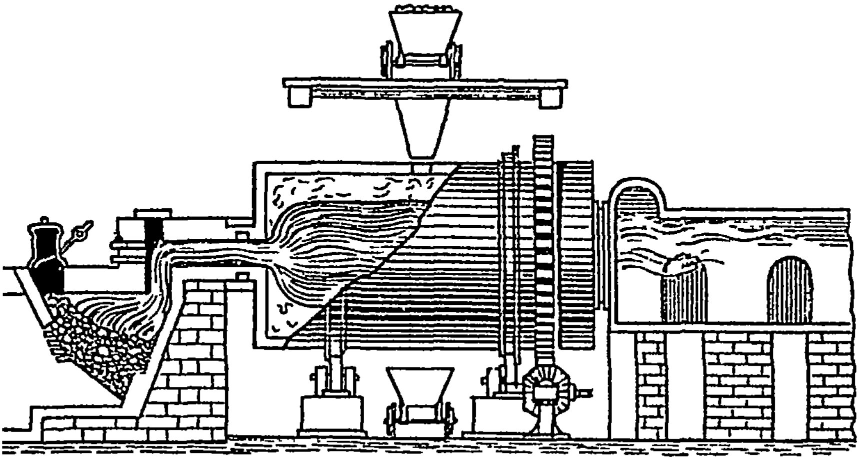


FIG 231.—Revolving Black Ash Furnace

the mass. The soda ash, Na_2CO_3, is then crystallized from water if soda crystals (washing soda) are wanted—$Na_2CO_3.10H_2O$.

The action of water on black ash during the washing involves a complex series of chemical changes. The free lime of the black ash reacts with the sodium carbonate, forming sodium hydroxide and calcium carbonate; the calcium sulphide reacts with sodium carbonate, forming sodium sulphide and calcium carbonate; the oxygen of the air oxidizes the calcium sulphide to calcium sulphate, which in turn reacts with sodium carbonate, etc. All these reactions reduce the yield from the process. The tank liquid is sometimes treated with carbon dioxide so as to convert the caustic soda and sodium sulphide into sodium carbonate.

4 **Recovery of sulphur from the tank waste by C F Claus and A M Chance's process**.—The residue in the tanks remaining after the sodium carbonate has been extracted is dried, finely powdered, and suspended in water. Carbon dioxide is forced through the liquid and hydrogen sulphide is driven off: $Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + 2H_2S$. The hydrogen sulphide mixed with sufficient oxygen to burn the hydrogen, but not the sulphur, is passed into a kiln containing iron oxide. By catalytic action, the iron oxide accelerates the oxidation of the hydrogen

sulphide $2H_2S + O_2 = 2H_2O + 2S$ Most of the sulphur which separates collects as a molten fluid at the bottom of the kiln or in an adjoining brickwork chamber, and is periodically run off About 85 per cent of the sulphur is thus recovered and used again for making sulphuric acid ' The oxide of iron is gradually converted into sulphide, and this is perhaps more efficient as a catalytic agent than the original oxide Tank waste can also be used for the manufacture of sodium thiosulphate (*q v*)

A factory in which soda ash is made is called an "alkali works" A works using the Leblanc process is divided into several departments (1) The acid works where sulphuric acid is made, (2) Salt-cake works, (3) Black-ash works and lixiviation, (4) White-ash (soda ash) works, (5) Bleaching powder works where the hydrogen chloride from the salt-cake works is converted into chlorine and the latter converted into bleaching powder, and (6) Sulphur extraction from tank waste

§ 11. The Ammonia-Soda or E Solvay's Process

This process depends upon the fact that when a concentrated solution of sodium chloride is saturated with ammonia, and carbon dioxide is passed through the mixture, sodium hydrogen carbonate is precipitated, and ammonium chloride remains in solution $NaCl + NH_4HCO_3 \rightleftharpoons NaHCO_3 + NH_4Cl$ If sodium carbonate is needed the bicarbonate is calcined $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$ This carbon dioxide forms part of that used in the first stage of the operation The mother liquid remaining after the separation of sodium bicarbonate is treated with lime obtained by burning limestone $CaCO_3 = CaO + CO_2$, and the ammonia is recovered ' $2NH_4Cl + CaO = CaCl_2 + H_2O + 2NH_3$ The ammonia and carbon dioxide evolved in these two operations are used again Thus calcium chloride is the only by-product which is not utilized The process can be illustrated by connecting an apparatus, *A*, for generating ammonia, Fig 235, and an apparatus, *B*, for making washed carbon dioxide with a tower, *C*, filled with a saturated solution of sodium chloride and fitted with four perforated iron discs as shown in the diagram The tower is provided with an exit tube dipping in a beaker of water The solution is first saturated with ammonia, and then with carbon dioxide In about an hour, crystals of sodium bicarbonate will be deposited on the perforated shelves

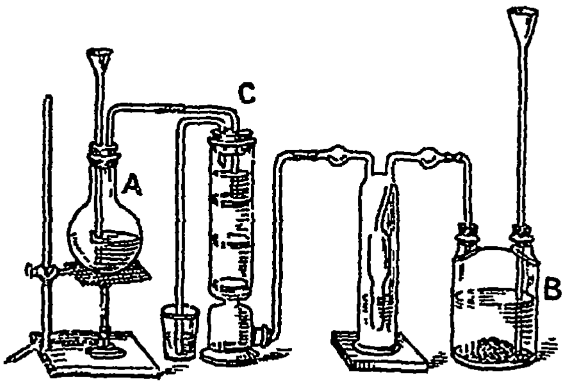


FIG 235 —Illustration of Solvay's Process

Potassium carbonate cannot be made by Solvay's process because acid potassium carbonate is too soluble A great deal of the potassium carbonate of commerce is made by Leblanc's process It is also made from the potassium chloride or sulphate of the Stassfurt deposits by forcing

carbon dioxide into a solution of potassium chloride containing magnesium chloride A complex double compound of magnesium carbonate and potassium hydrogen carbonate is formed This is decomposed by steam, the magnesium is precipitated as hydroxide, and the clear solution is evaporated for potassium carbonate.

§ 12 Percarbonates

E J Constam and A von Hansen (1896) found that when a saturated aqueous solution of potassium carbonate is electrolyzed at a temperature below $-10°$, a sky blue precipitate separates, which, when dried over phosphorus pentoxide, is nearly white The precipitate is a mixture of potassium carbonate and potassium percarbonate—$K_2C_2O_6$ or KCO_3, which may be graphically represented by one of the formulæ

$$O{=}C{<}^{OK\ \ KO}_{O\text{———}O}{>}C{=}O \quad \text{or} \quad O{=}C{<}^{O-OK\ \ KO}_{\text{———}O\text{———}}{>}C{=}O$$

which recalls that given above for acid calcium carbonate Neither the acid $H_2C_2O_6$, nor the anhydride C_2O_5 has been isolated The percarbonate decomposes on gentle warming, giving potassium carbonate and a mixture of carbon dioxide and oxygen $2K_2C_2O_6 = 2K_2CO_3 + 2CO_2 + O_2$ It furnishes hydrogen peroxide when treated with dilute sulphuric acid or dilute alkalies $K_2C_2O_6 + 2H_2SO_4 = 2KHSO_4 + 2CO_2 + H_2O_2$, $K_2C_2O_6 + 2KOH = 2K_2CO_3 + H_2O_2$ The salt thus acts as a strong oxidizing agent like hydrogen peroxide For instance, it converts lead sulphide (PbS) into lead sulphate ($PbSO_4$), bleaches indigo, etc It forms with manganese and lead dioxides the corresponding carbonates, and at the same time reduces the dioxide $PbO_2 + K_2C_2O_6 = PbCO_3 + K_2CO_3 + O_2$ The dry salt keeps unchanged for an indefinite period, and some accordingly prefer potassium percarbonate to less stable salts as a source of hydrogen peroxide in certain analytical operations oxidation of sulphides to sulphates, chromic salts to chromates, hypochlorites to chlorides, titanium and vanadium to the coloured peroxides, etc A similar compound, isomeric with $K_2C_2O_6$ prepared by electrolysis, can be made by the action of carbon dioxide on a cold solution of sodium peroxide This compound behaves differently towards a solution of potassium iodide whether added as solid or as a solution, and differently from the percarbonate prepared by electrolysis.

S Tanater (1899) prepared yet a third percarbonate by dissolving an alkaline carbonate in a 3 per cent solution of hydrogen peroxide, and after a few minutes, precipitating the salt by the addition of ether The same salt is obtained by the action of carbon dioxide on a solution of, say, sodium peroxide in water The salt has the ultimate composition Na_2CO_4 Just as the acid H_2CO_3 corresponds with sulphurous acid H_2SO_3, so the salt Na_2CO_4 might be supposed, at first sight, to correspond with salts of sulphuric acid—H_2SO_4, but the constitution of Tanater's percarbonate is generally taken to be

$$O{=}C{<}^{ONa}_{O-ONa}$$

Salts of the type Na_2CO_4 are called monoperoxycarbonates, and salts of the type $Na_2C_2O_6$ are called monoperoxydicarbonates The acid

corresponding with H_2CO_4 has not been prepared The aqueous solutions of the salt Na_2CO_4 readily decompose into sodium carbonate and hydrogen peroxide On heating, the salt forms sodium carbonate and oxygen, but no carbon dioxide

Some of the so-called percarbonates prepared by the action of hydrogen peroxide on the carbonates seem to contain "hydrogen peroxide of crystallization"—*e g* $Rb_2CO_3 \, 3H_2O_2$—and these salts liberate very little iodine from a neutral solution of potassium iodide under conditions where the true percarbonates give a quantitative yield of iodine. It may be added, *en passant*, that similar remarks apply to the sulphates and persulphates Hence, a distinction must be drawn between the true peroxy-salts, and salts containing hydrogen peroxide of crystallization

§ 13 The Solubility of Gases in Liquids

Our study of the solubility of gases in liquids (p 158) may now be resumed The solubility depends upon the nature of the gas and of the solvent, as well as upon the temperature and pressure of the system. No "common" solubility has been observed, and we have no generalization of such wide applicability as Boyle's and Charles' laws Some gases are only slightly soluble in water, others dissolve very copiously One volume of water, at normal temperature and pressure, will dissolve 1200 volumes of ammonia, and but 0 021 volume of hydrogen

Kinetic theory of gaseous solution —The kinetic theory of gases furnishes a mental picture of the process of solution of a gas in water. Suppose that a gas free liquid be brought into a vessel containing a gas The molecules of gas impinging upon the surface of the liquid will be absorbed The dissolved molecules move about in the liquid in all directions, a small number escape back into the gas above As the molecules of the gas crowd more and more in the liquid, the number of molecules absorbed by the liquid becomes more and more nearly equal to the number which escapes back into the superincumbent gas If the pressure of the gas remains constant, a time will come when the number of gas molecules which leave the liquid will be equal to the number absorbed The system is then in a state of dynamic equilibrium resembling the equilibrium of a vapour in contact with its own liquid, and the solution is saturated with the gas under the given conditions of temperature and pressure

$$O_2 \text{ gas} \rightleftharpoons O_2 \text{ sol}$$

The surface of the liquid in contact with a dissolving gas must be very quickly saturated with the gas, and the rate of absorption of a gas by a liquid at rest is really a measure of the rate of diffusion of the gas from the surface through the body of the liquid The molecules of the liquid must have some attractive influence on the molecules of the dissolved gas [1]

Influence of pressure —With gases which are not very soluble in liquids, the greater the pressure, the more soluble the gas, that is, the greater the pressure, the greater the concentration of the gas in the solution W Henry (1803) discovered an important relation between the

[1] It is probable that the attractive forces between the molecules of the liquid and the dissolving gas determine the coefficient of solubility of the different gases, otherwise we should expect the solubility of certain groups of gases to be the same.

pressure and the solubility of a gas Under a total pressure, p, of 2 atmospheres, a saturated solution of gas holds in solution twice as much gas by weight, w, as under a total pressure of 1 atmosphere Otherwise expressed, w/p = a constant. According to Boyle's law, the concentration of a gas, or the amount of gas w in an enclosed space, is proportional to the pressure One volume of a gas at atmospheric pressure will make half a volume of gas at a pressure of 2 atmospheres Under a pressure of 4 atmospheres, a saturated solution of gas holds four times as much gas in solution as it did under a pressure of 1 atmosphere, but four volumes of gas at atmospheric pressure occupy but one volume at a pressure of 4 atmospheres Hence follows Henry's law "under equal circumstances of temperature, water takes up in all cases the same volume (c) of a condensed gas as of gas under ordinary pressure" That is to say, c/p = a constant The law thus describes the behaviour of the less soluble gases very well—carbon monoxide, nitrogen, hydrogen, oxygen—but not the more soluble gases like ammonia, hydrogen chloride, sulphur dioxide The deviation is not very great with carbon dioxide, though it is appreciable

Pressure (p)	1	5	10	15	20	25	30	atms
Solubility (c)	1 80	8 65	16 03	21 95	26 65	30 55	33 74	vols per c c
c/p	1 80	1 73	1 60	1 46	1 33	1 22	1 12	

The graph, Fig 236, represents the observed values of p and c, and the dotted curve in the same diagram represents what the graph would have been had carbon dioxide behaved as described by Henry's law The value of c/p is not therefore quite constant The failure arises from the fact that carbon dioxide reacts chemically with water Henry's law refers (1) to gases which do not act chemically on the solvent When carbon dioxide dissolves in water, one portion enters into combination to produce a new substance—carbonic acid—while the other portion dissolves in the physical sense as carbon dioxide The latter portion alone comes within the province of Henry's law The condition of the carbon dioxide dissolved by the water is therefore represented by $CO_2 + H_2O \rightleftharpoons H_2CO_3$

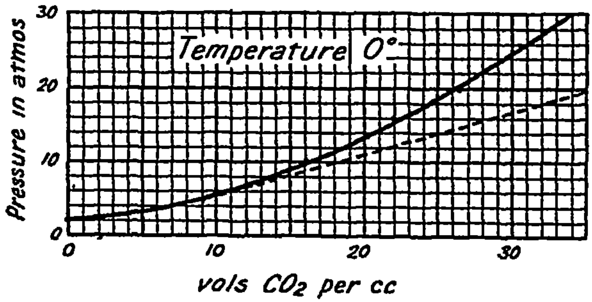


FIG 236—Solubility Curve of CO_2 in Water

Henry's law also assumes (2) that the molecules of the dissolved gas are no heavier than the molecules of the gas itself Hence it may be inferred that if a gas "obeys" Henry's law, it will have the same molecular weight in solution and in the gaseous condition Henry's law is therefore to be regarded as a link connecting the molecular weights of gaseous and dissolved substances with one unit of measurement If 32 grams of oxygen depress the freezing point to the same extent as 342 2 grams of cane sugar, it is inferred that the molecular

weights of oxygen and cane sugar are related as 32 : 342.2, and since oxygen gas has a molecular weight of 32, it is assumed that cane sugar if it could be vaporized, and if its gas obeyed Henry's law, would have a molecular weight of 342.2, because, as indicated above, the molecular weights of a substance in solution and in the gaseous state are the same.

Henry's law and the kinetic theory.—The gas is in equilibrium with its own solution when the number of molecules which escape from the solution is the same as those which are captured by the solution in a given time. By, say, doubling the pressure the molecular concentration will be doubled, the gas molecules will be crowded more closely together, and the rate at which the solution captures the molecules will be increased twofold for the new state of equilibrium. Similarly the rate of escape will be doubled, and consequently the number of dissolved molecules will be doubled. Hence variations of pressure do not alter the relative number of molecules per unit volume of solution and of gas; and the *volume* of gas dissolved will be independent of the pressure on the gas, while the *weight* of gas dissolved will be directly proportional to the pressure.

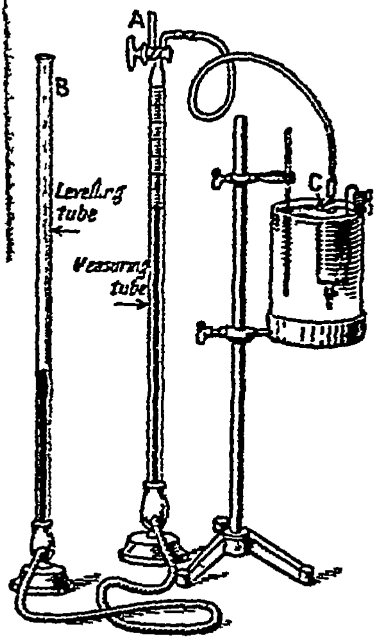


FIG. 237.—Determination of the Solubility of Gases.

Measuring the solubility of gases.—The solubility of gases in a liquid can be conveniently determined in the following apparatus, modified from that used by R. Heidenhain and L. Meyer (1863). The pipette *C* (Fig. 237) is filled with a measured volume of the liquid under investigation. It is connected with a Hempel's burette by means of a piece of metal tubing of narrow bore. The gas under investigation is introduced into the measuring tube *A*, *via* the three-way cocks *C* and *A*, by first raising and then lowering the levelling tube *B*. A definite volume of liquid is then run from the pipette *C* by opening the lower cock and putting the pipette *C* in communication with the burette. A certain amount of gas enters the pipette. The contents of the pipette are then agitated and when all is in equilibrium, and the liquid is saturated and the mercury in the burette and levelling tube are at a constant level, place the lower end of the absorption pipette beneath a vessel of mercury, and bring the liquid in the pipette to its former level. The diminution of the volume of gas in the burette represents the volume of gas absorbed by the volume of liquid in the pipette at the temperature and barometric pressure at the time of the experiment. To vary the temperature of absorption, the burette and pipette must be kept in a liquid or vapour bath at the desired temperature, and the measurements made when everything is in equilibrium.

It might be emphasized, in passing, that when a gas is dissolved in a liquid at a given *temperature*, the ratio between the concentration of the gas in the liquid and in the space above is always the same. Thus Henry's

law is a law of distribution for gases because it describes the way a gas distributes itself between the solvent and the space above Henry's law also describes the condition of equilibrium of a gas whose molecules are physically and chemically independent of each other, and of the solvent

The influence of temperature —The solubility of a gas in a liquid is very sensitive to changes of temperature The higher the temperature, the less the solubility of the gas. The solubility curve for helium is not much affected by changes of temperature up to 50°, but what little effect there is seems to indicate that the solubility of the gas *increases* as the temperature rises from 25° to 50° Hydrogen was once supposed to behave in a similar way, between 0° and 25°, but later, more careful measurements show that the solubility decreases steadily from 0 0214 at 0° to 0 0171 at 26°

§ 14 The Solubility of Mixed Gases—Dalton's Law

When a mixture of two gases is exposed to the action of a solvent, the quantity of each gas dissolved by the liquid depends upon the amount and the solubility of each gas present The amount of each gas determines its partial pressure, and since the partial pressure of each gas is independent of the others, it follows that when a mixture of gases is exposed to the action of a solvent, the amount of each gas which is dissolved by the solvent is proportional to the partial pressure of the gas Each gas behaves as if the others were absent This is Dalton's law *It is a simple extension of Henry's law*

Application to air —When air containing, say, 79 volumes of nitrogen[1] and 21 volumes of oxygen, and 0·04 volumes of carbon dioxide, is shaken up with water, the amount of each gas absorbed by the water can be approximately computed in the following manner The relative solubilities are nitrogen, 0 02, oxygen, 0 04, and carbon dioxide, 1 79 The partial pressure of each gas is proportional to the relative amount of that gas present in a given volume of air If the pressure of air be just one atmosphere, the partial pressure of the nitrogen will be proportional to $0\ 79 \times 1$, of oxygen $0\ 21 \times 1$, and of carbon dioxide, $0\ 0004 \times 1$ Hence the relative amounts of these gases absorbed by the water will be nitrogen, $0\ 79 \times 0\ 02 = 0\ 0158$, oxygen, $0\ 21 \times 0\ 04 = 0\ 0082$, and carbon dioxide, $0\ 0004 \times 1\ 79 = 0\ 00072$ Hence 1 c c of water dissolves 0 0158 c c of nitrogen, 0 0082 c c of oxygen, and 0 00072 c c of carbon dioxide The composition of the dissolved gases, if removed from the air by boiling, or exposure to a vacuum, will be nitrogen, 63 9 per cent., oxygen, 33 2 per cent., carbon dioxide, 2 9 per cent The relatively large solubility of carbon dioxide is counterbalanced by its low partial pressure, otherwise we might expect a heavy rain storm to remove a great part of the carbon dioxide from the atmosphere Mallet has based a proposal to separate oxygen from atmospheric air on the action If the carbon dioxide be removed by passing the air through an aqueous solution of sodium hydroxide, the oxygen and nitrogen in the remaining gases after the first absorption will be nearly in the proportion nitrogen 65 7 per cent, and oxygen 34 3 per cent If this mixture be driven from the water by boiling, and the mixture again treated

[1] Neglecting argon, etc.

with air-free water, a gaseous mixture containing 40 per cent of oxygen is obtained, and after the eighth absorption, a gas containing 98 per cent of oxygen results. The method is not practicable though it is an interesting application of Henry's and Dalton's laws

EXAMPLES —(1) If a litre of water dissolves 25 12 c c of air, show that the mixture of gases obtained by boiling this water will contain 8 2 c c of oxygen; 15 8 c c of nitrogen and 0 72 c c of carbon dioxide

(2) Show that the mixture of gases expelled from water on boiling is between 71 and 72 times as rich in carbon dioxide as normal air

According to Wroblewsky, the crystalline hydrate, CO_2 $8H_2O$, is formed when aqueous solutions of carbon dioxide at 0° are subjected to a pressure of 12 atmospheres

§ 15 Van der Waals' attempt to obtain a more exact Gas Equation.

We have seen that the gas equation does not describe the behaviour of real gases with respect to changes in volume with variations of temperature and pressure. The same gas does not behave in the same way at high and at low pressures For many gases—hydrogen, oxygen, etc — the laws of Boyle and of Charles are fairly exact at temperatures and pressures not far removed from normal atmospheric conditions, and

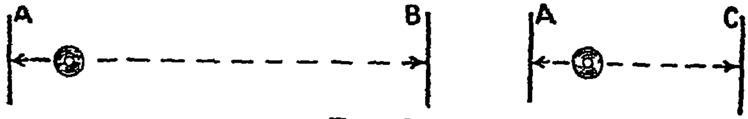


FIG 238

where they are not—carbon dioxide, ethylene, etc.—it is often convenient to neglect the small deviations. This means that gas calculations with $pv = RT$ are made upon imaginary gases, sometimes styled *ideal or perfect gases* When the pressure upon the gas is very great, the error becomes quite appreciable, and it is necessary to revise the simple gas law: $pv = RT$.

(1) Molecular co-volume —Let b denote the space occupied by the molecule as it moves to and fro between the boundary walls AB, Fig 238 If this distance be halved, AC, Fig 238, while the volume of the molecule remains constant, the molecule will have *less* than half its former distance to pass from one side to the other[1] It will therefore strike the walls more frequently than before Hence the outward pressure of the molecule will increase more rapidly with decreasing volume than is described by Boyle's law Boyle's law refers to the whole volume of the gas, but rather should it refer to the space in which the molecules move. We therefore write $v - b$ in place of v in Boyle's law, and the result is.

$$p(v - b) = RT$$

where b is called the "co-volume" or "vibratory volume" of the molecule.[2]

[1] *E g* suppose AB represents two units, and the diameter of the molecule $\frac{1}{10}$ unit, the molecule then moves through 1 9 units of space, and in AC through 0 90 unit, not 0 95 unit, in passing from one boundary wall to the other

[2] A study of the kinetic theory has led to the view that b is relatively near four times the material volume of the molecule A molecule seems to be a complex vibratory system with a material nucleus, ¼b in size, which requires b volumes of space in which to perform its oscillatory movements Hence, b is sometimes called the "vibratory volume" of the molecule

(2) **Molecular attraction.**—The closer proximity of the molecules to one another, the greater will be the effect of the attractive forces between the molecules. This attractive force will tend to make the gas occupy a smaller volume. The effect is much the same as if the gas were subjected to the action of a greater external pressure than the observed or apparent pressure of the gas. The assumption that the attractive force between the molecules varies inversely as the fourth power of the distance between the molecules leads to a/v^2 as the magnitude of the molecular attraction, where a is a constant which varies with the nature of the gas. Granting the assumption, a/v^2 must therefore be added to the observed pressure of the gas in order to indicate the total pressure tending to compress the gas. On correcting the equation $pv = RT$ for the volume and the cohesion of the molecules, we obtain the so called J. D. van der Waals' equation (1872)

$$\left(p + \frac{a}{v^2}\right)\left(v - b\right) = RT$$

This amended equation agrees fairly well with a number of observations of gases under large pressures, and of gases which are near their points of liquefaction—e.g. ethylene, carbon dioxide, etc. It also describes many of the properties of liquids, and of the continuous passage of a gas to the liquid condition. The constants a and b must be evaluated from observations. Their numerical value is not quite constant at different temperatures. Quite a number of attempts have been made to still further modify the gas equation so that it may describe the behaviour of gases under wide variations of pressure and temperature. J. D. van der Waals (1888) found that for carbon dioxide, $R = 0.00369$, $b = 0.0023$, and $a = 0.00874$. On comparing the values of pv for carbon dioxide, calculated from the equation, at 20°

$$\left(p + \frac{0.00874}{v^2}\right)\left(v - 0.0023\right) = 1.08$$

with the numbers observed by E. H. Amagat (1893) at 20°, we get

p atmospheres	pv Observed	pv Calculated
1	1.000	1.000
50	0.680	0.678
75	0.180	0.179
100	0.228	0.226
200	0.419	0.411
500	0.938	0.936

It will be observed that if the gas behaves according to the equation $pv = RT$, pv would have the same value for all pressures. As a matter of fact, the value of pv first decreases and then increases for all gases except hydrogen and helium. The two corrections act in opposite ways. At first the value of pv is decreased by the molecular attraction, and increased by the finite dimensions of the molecule. At low pressures the correction for molecular attraction preponderates over that required for the volume

of the molecule, while the correction for the volume of the molecules is relatively large when the volume of the gas is compressed very small by a large pressure (Cf pp 79, 85) Several attempts have been made to still further improve the gas equation by the introduction of other terms, involving special constants which have to be evaluated from the experimental numbers They are therefore of very limited application

§ 16 The Critical State of Gases.

In 1869 T Andrews found that if carbon dioxide be gradually compressed in a vessel suitable for the observation, the volume diminishes more rapidly than would occur if Boyle's law correctly described the behaviour of the gas, and when the pressure attains a certain value, the gas begins to liquefy A further decrease in the volume does not change the pressure, but only increases the quantity of gas liquefied. At length, when all the gas has liquefied, a large increase of pressure only causes a minute decrease in the volume of the liquid, since liquids in general undergo but a small change of volume on compression

If the experiment be made with carbon dioxide at 0°, the gas commences to liquefy when the pressure has attained 35 4 atmospheres, if at 13 1°, liquefaction commences at 48 9 atmospheres pressure, if at 30°, at 70 atmospheres pressure, while if the temperature exceeds 31°, no pressure, however great, will liquefy the gas Other gases exhibit similar phenomena For each gas there is a particular temperature above which liquefaction is impossible, Andrews called this the critical temperature of the gas For instance, the critical temperature of

Hydrogen	−241°	Nitrous oxide	+35°
Nitrogen	−146°	Ammonia	+130°
Oxygen	−119°	Sulphur dioxide	+155°
Carbon dioxide	+31°	Water	+358°

It is interesting to notice the influence of temperature on carbon dioxide, partly liquid, partly gaseous Fig 239, *A*, represents the upper end of a glass tube in which the partly liquefied carbon dioxide is confined over mercury, at 18° The surface of the liquid has a sharply defined curved meniscus. On raising the temperature, the meniscus of the liquid becomes flatter and flatter, Fig 239, *B*, until, at 31°, Fig 239, *C*, the surface seems to disappear The sharp line of demarcation between the liquid and the gas vanishes. At 40°, the tube contains a homogeneous gas, Fig 239, *D* Liquid carbon dioxide cannot exist at this temperature, however great the pressure

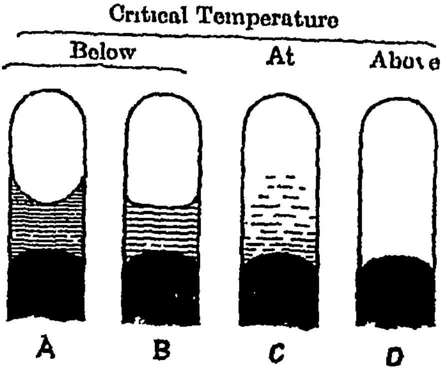


FIG 239 —Diagrammatic Illustration of the Critical State of a Gas

The relation between the pressure and the volume of, say, carbon dioxide, at different temperatures—T, T_0, T_1, T_2—is represented diagrammatically in Fig 240 The portion of the curve K_2T_2, or K_1T_1, represents the behaviour of the gas when no liquid is present, the portion

K_2M_2, or K_1M_1, the behaviour of the gas in the presence of its own liquid, and M_2p_2, or M_1p_1, the behaviour of the liquid when no gas is present. It will be observed that K_2M_2 or K_1M_1 is a straight line horizontal with the v axis It illustrates in a graphic manner the well known law At any fixed temperature, the pressure of a gas in the presence of its own liquid is always the same The curve $T_0K_0p_0$ represents the relation between pressure and volume at the critical temperature, and the curve T, the relation between p and v at a temperature when the gas does not liquefy The line $K_0K_1K_2B$ represents the condition under which the gas, compressed at the stated temperatures T_0, T_1, T_2, begins to liquefy, and it is hence called the dew curve, because a gas under a gradually increasing pressure first shows signs of liquefaction under conditions represented by a point on this line, similarly, the line $K_0M_1M_2A$ is called the boiling curve, because a liquid, under a gradually diminishing pressure, first shows signs of vaporization under conditions represented by a point on this line Note also that the lines K_0A, K_0B, and K_0p_0, divide the plane of the paper into three regions Every point to the right of BK_0p_0 represents a homogeneous gas, every point in the region AK_0B represents a heterogeneous mixture of gas and liquid, and every point to the left of AK_0p_0, a homogeneous liquid The diagram, Fig 240, thus represents the conditions of equilibrium of a liquid or a gas under different conditions of temperature, pressure or volume

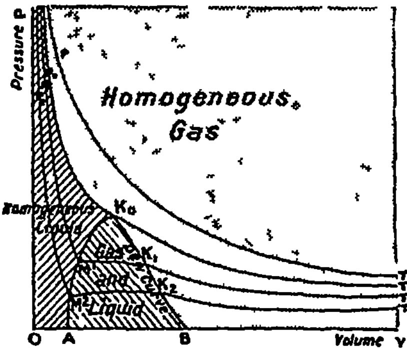


FIG 240 —$p : v$—Curves for Carbon Dioxide

It is interesting to note historically that Caignard de la Tour, long before Andrews' experiment, noticed that when a liquid is heated in a sealed tube there is a definite temperature at which the surface of separation between the gas and liquid disappeared, and the whole contents of the tube become homogeneous. Caignard de la Tour's experiments thus demonstrate that the critical temperature is the upper limit to the liquid state, and Andrews' experiments prove that the critical temperature is the lower limit to the gaseous state The passage from the one state to the other proceeds in a continuous manner The liquid and gaseous states are continuous, not abrupt The properties—density, surface tension, viscosity, refractive power, heat of vaporization, compressibility, etc.—of a liquid gradually lose their distinctive character as the temperature is raised, until, at the critical temperature, the properties of liquid and gas are the same There is no evidence of a change in molecular structure when, say, carbon dioxide passes from the one state of aggregation to the other There is no evidence of a polymerization of the molecules [1]

[1] Nitrogen peroxide, water, and some other substances appear to polymerize and form compound molecules on passing from the gaseous to the liquid state of aggression The properties of the condensing gases do not then exhibit that continuity shown by carbon dioxide and gases which do not polymerize

when the common gases condense to liquids. The difference between liquids and gases *below* the critical temperature seems to be a question of molecular attraction.

§ 17 Carbon Monoxide—Preparation and Occurrence

Molecular weight, CO = 28 Melting point, −203°, boiling point, −190°, critical temperature, −139 5° Relative vapour density (H_2 = 2), 27 81, (air = 1) 0 9672

Two oxides of carbon are very well known—carbon monoxide and carbon dioxide In the section dealing with producer gas, p 711, it will be shown that the former is partially burnt or oxidized carbon, and is formed when carbon is heated in a limited supply of air $2C + O_2 = 2CO$ It is also produced when carbon dioxide is heated in the presence of an excess of carbon $CO_2 + C = 2CO$ Carbon dioxide is reduced in a similar manner when passed over hot metallic zinc $CO_2 + Zn = ZnO + CO$ If zinc oxide be reduced with carbon, metallic zinc and carbon monoxide are produced $ZnO + C = Zn + CO$ F de Lassone first made carbon monoxide by this reaction in 1776, and Priestley prepared it by heating iron oxide with charcoal in 1796 Lavoisier knew that this gas burned to carbon dioxide, but he was not able to satisfactorily fit carbon monoxide in with his theory of oxidation This became possible when W. Cruickshank, in 1800, showed that the gas was nothing but a "gaseous oxide of carbon," and F Clément and J B Désormes, in 1801, made clear the composition of the gas

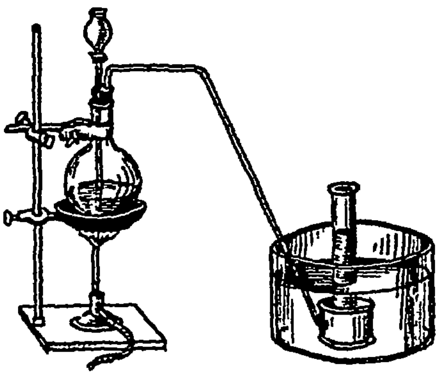


FIG 241 —Preparation of Carbon Monoxide

Carbon monoxide seldom occurs free in nature and then only in small quantities. Minute traces have been detected in air, in volcanic gases, occluded in coal, and in meteorites. It is found in tobacco smoke in chimney gases where the air is not in a sufficiently large excess, and in the gases from blast and other furnaces

Preparation —Carbon monoxide is best made in the laboratory by heating concentrated sulphuric acid to about 100° in a flask (Fig 241), fitted with a double-bored rubber stopper, one hole of the stopper is fitted with a gas delivery tube, and the other with a tap funnel containing concentrated (98 per cent) formic acid. Each drop of formic acid produces some bubbles of gas The reaction is simple $H.COOH + H_2SO_4 = H_2SO_4 H_2O + CO$ There is no frothing, and the velocity of the stream of gas can be regulated by the rate at which formic acid is dropped on to the sulphuric acid. Concentrated sulphuric acid can also be mixed with sodium formate in a flask provided with a safety funnel, and very gently warmed Carbon monoxide is evolved

The gas is also made by gently heating 20 to 30 grams of crystalline oxalic acid just covered with concentrated sulphuric acid The rate of evolution of the gas is determined by the temperature of the mixture Equal volumes of carbon dioxide and carbon monoxide are produced The former is removed by passing the gas through a series of wash-bottles containing a solution of caustic soda,

This process is more troublesome than the formic acid process The same remark applies to the preparation of carbon monoxide by heating say, 30 grams of crystalline potassium ferrocyanide with 100 c c of concentrated sulphuric acid in a capacious flask In this case the temperature of decomposition is high, and if the mixture be heated too quickly, the gas is apt to come off so quickly as to be beyond control If dilute sulphuric acid be used hydrocyanic acid as well as carbon monoxide may be formed The reaction in the latter case is represented $2K_4FeCy_6 + 3H_2SO_4 \rightarrow 3K_2SO_4 + K_2Fe_2Cy_6 + 6HCy$

§ 18 The Properties of Carbon Monoxide

Carbon monoxide is a colourless, tasteless, and odourless (poisonous) gas One volume of water dissolves about 0·03 volume at 0°, and about 0 023 volume at 20° The gas condenses to a colourless transparent liquid at −190°, at atmospheric pressure, the liquid solidifies at −203° When a lighted taper is plunged into the gas, the taper is extinguished (non supporter of combustion), but the gas is inflamed (combustible), and burns with a blue flame The blue lambent flame which appears on the surface of a clear red coke (or coal) fire, or over the ignited lime in a lime kiln, is carbon monoxide If a beaker be held over a burning jet of carbon monoxide for a moment, and clear lime water be poured into the beaker, a turbidity shows the presence of carbon dioxide Carbon monoxide, on burning, forms carbon dioxide $2CO + O_2 = 2CO_2$ Collect a mixture of two volumes of carbon monoxide and one volume of oxygen in a soda water bottle apply a lighted taper to the mouth of the bottle, the mixture explodes with some violence If the gases be thoroughly dried by means of phosphorus pentoxide a spark can pass through the mixture of two volumes of carbon monoxide and one volume of oxygen without explosion There appears to be a slight combination, but only in the path of the spark H B Dixon showed that the presence of gases containing hydrogen—hydrogen sulphide, pentane, ammonia, etc —act like water, and make the mixture explosive, whereas gases not containing hydrogen—sulphur dioxide, carbon disulphide, etc —are inert, for the mixture does not explode Water thus appears to act as a catalytic agent, and Dixon thinks that there is a cyclic process (p 130) involving the reactions

$$CO + H_2O = CO_2 + H_2,\ 2H_2 + O_2 = 2H_2O,\ CO + H_2O = CO_2 + H_2$$

This emphasizes how even the so called simple reactions are much more interesting than the ordinary chemical equations would lead us to suppose How much more wonderful must be the reactions which are now represented by more complex equations If moist carbon monoxide be passed over palladium black in the cold, formic acid, H CO OH, can be detected among the products of the action The end products of the reaction are hydrogen and carbon dioxide—the hydrogen is largely retained by the palladium If the flame of burning carbon monoxide be allowed to play upon ice, formic acid can be detected in the water formed by the melting ice Hence it is assumed that the first stage of the reaction is $H_2O + CO = H\,COOH$, followed by $H\,COOH = H_2 + CO_2$ The formic acid is an intermediate product of the two consecutive reactions (p 130) The reverse reaction, reduction of carbon dioxide to formic acid $CO_2 + H_2 \rightleftharpoons H\,COOH$, occurs under the influence of palladium black

Carbon monoxide is not absorbed by solutions of potassium or sodium hydroxide (distinction from carbon dioxide) Unlike carbon dioxide, carbon monoxide is soluble in a saturated solution of cuprous chloride

in concentrated hydrochloric acid, or of cuprous chloride in ammonia. Hence these solutions are used as absorbents for carbon monoxide in gas analysis Some suppose that the carbon monoxide unites with the cuprous chloride, forming a compound $2CuCl\ CO\ 2H_2O$

Action on iron —Carbon monoxide is an important reducing agent, ferric oxide, for instance, is reduced to the metal in the blast furnace: $Fe_2O_3 + 3CO = 2Fe + 3CO_2$. The action is, however, somewhat complex, and dependent upon the temperature When metallic iron is heated in a current of carbon monoxide at about 330°, the carbon monoxide is decomposed, forming ferrous oxide and carbon $Fe + CO = FeO + C$ (+ 20 1 Cals.) At higher temperatures the ferrous oxide is reduced to the metal by this gas $FeO + CO = Fe + CO_2$. At 400° the former reaction is about twelve times as fast as the second As the temperature is raised, the speed of the latter reaction is accelerated until it appears as if the ferric oxide were directly reduced by the carbon monoxide, any ferrous oxide formed is at once reduced. This is a curious example of consecutive reactions discussed on p 135 T Graham showed that metallic iron absorbs about four times its volume of carbon monoxide at a dull red heat, and the gas is given off when the metal is heated in air Hence iron appears to be permeable to carbon monoxide, and if this gas be passing up a hot stove pipe, with the flue gases, some carbon monoxide could pass through the metallic iron into the atmosphere of the room.

Composition —A mixture of carbon monoxide and oxygen can be exploded in the apparatus illustrated in Fig 189 It will be found that 100 vols. of carbon monoxide with 100 vols of oxygen gave 150 vols of gas. When the gaseous product of the explosion was treated with a solution of potassium hydroxide 50 vols of oxygen remained The absorption was conducted as indicated on p 661, Fig 231 This shows that 100 vols. of carbon monoxide combined with 50 vols of oxygen to form 100 vols of carbon dioxide. By Avogadro's hypothesis, this agrees with the equation $2CO + O_2 = 2CO_2$. The density of the gas is nearly fourteen times that of hydrogen Hence the molecular weight of the gas is 28 (hydrogen = 2) The atomic weight of carbon is 12, and oxygen 16, and 12 + 16 = 28 Hence CO, not C_2O_2, C_3O_3 . . . is the correct formula for carbon monoxide

Carbon monoxide—a poison —Carbon monoxide is an active poison When it is respired in the lungs, it unites with the hæmoglobin of the blood, forming a bright cherry-red coloured compound carbonyl-hæmoglobin which prevents the hæmoglobin performing its regular work of oxidizing waste tissue (p 738) Less than 1 per cent. in the atmosphere is sufficient to cause death when inhaled. J S Haldane says that air containing $\frac{1}{20}$ of one per cent of carbon monoxide will produce giddiness on exertion if breathed for from one-half to two hours, and $\frac{1}{10}$ per cent makes one unable to walk, $\frac{1}{5}$ per cent leads to loss of consciousness and perhaps death, $\frac{2}{5}$ per cent means probable death, and 1 per cent will lead to unconsciousness in a few minutes, followed before long by death.[1] Fatal accidents have arisen from the breathing of carbon

[1] First aid treatment for carbon monoxide poisoning, or "gassing," as it is often called, is artificial respiration at once, accompanied by the use of oxygen for about 10 minutes A person seriously gassed should be kept warm and protected from cold air he should not exert himself by walking, and if there is a tendency to fainting, a little brandy or whisky should be administered.

monoxide, when its presence has not been suspected. It is formed when a gas flame is exposed to a cold surface as might occur in some "patent water heaters" used in ill ventilated bathrooms, etc in slow combustion stoves, and charcoal pans. It is often present in rooms where gas producers are at work (p 711), and in rooms with an escape of coal gas, water gas, etc The poisonous character of "after damp" in coal mines is due to the presence of some carbon monoxide along with the carbon dioxide formed during an explosion of firedamp or coal dust in air after the use of explosives for blasting, underground fires, etc J S Haldane recommends miners to carry a mouse in an open cage in a suspected atmosphere As soon as the mouse shows signs of sluggishness or exhaustion, a dangerous amount of carbon monoxide is probably present

Testing for carbon monoxide —The detection of carbon monoxide is not easy A piece of white filter paper moistened with palladium chloride —$PdCl_2$—is turned pink, green, or black, according to the amount of carbon monoxide present in the atmosphere But other organic substances produce the same reaction, and mistakes might easily be made Vogel's blood test is considered the most reliable If ordinary blood be diluted with 200 times its volume of water, a yellowish red solution is obtained, with blood containing carbon monoxide, the solution is distinctly pink. J S Haldane recommends placing a mouse in the suspected atmosphere for, say, fifteen minutes It is then killed. A known volume of the blood drawn from the heart of the mouse is then systematically diluted, simultaneously with another sample of ordinary oxygenated blood, until the tints of both solutions appear the same in daylight A comparison of the amount of blood in the two solutions will give a rough idea of the amount of carbon monoxide in the air since it is found that the blood of the mouse 20 per cent. saturated represents 0 02 per cent. of carbon monoxide, 33 per cent. saturated with 0 04 per cent carbon monoxide, 50 per cent saturated with 0 08 per cent. of carbon monoxide, 66 per cent saturated with 0 16 per cent carbon monoxide in the air

Carbon suboxide —Certain other oxides of carbon have been reported by B C Brodie (1873), M. Berthelot (1876), etc (1) Brodie's oxide, C_4O_3, is formed as a reddish brown mass by exposing carbon monoxide to the prolonged action of the electric discharge, (2) Berthelot's oxide, C_8O_3, is formed as a dark brown mass by heating Brodie's oxide between 300° and 400°, and (3) Diels' carbon suboxide, C_3O_2, has been made by O Diels (1906) by distilling malonic acid, $CH_2(COOH)_2$, or its (ethereal) salts with a large excess of phosphorus pentoxide under reduced pressure (12 mm. mercury) at about 300° The gases are cooled so as to remove the unchanged acid, carbon dioxide, ethylene, etc The reaction is represented $CH_2(COOH)_2 = 2H_2O + C_3O_2$. When passed through a tube dipping in liquid air, a white solid with a pungent odour is obtained The solid melts between −107° and −108° and boils at 7° When treated with water, carbon suboxide re-forms malonic acid, and hence this oxide is regarded as malonic anhydride. The suboxide is combustible and burns with a blue smoky flame, forming carbon dioxide The vapour and liquid polymerize at ordinary temperatures, forming a dark red solid soluble in water The suboxide decomposes rapidly at 37° and instantaneously at 100° Analysis by combustion with copper monoxide, by explosion with

oxygen, and vapour density determinations by Hofmann's method all correspond with the formula C_3O_2 The constitution is uncertain, it is generally supposed to be represented by O=C=C=C=O, or by $C\overset{\displaystyle C}{\underset{\displaystyle CO}{\lessgtr}}O$ An oxide, C_3O_2, has also been formed by the action of the silent electric discharge on carbon monoxide $4CO = C_3O_2 + CO_2$ There is little doubt about the existence of carbon suboxide C_3O_2, but the identity of the other oxides—C_8O_3, and C_4O_3—is not well established

§ 19 Carbonyls.

According to the valency hypothesis, oxygen a dyad and carbon a tetrad, carbon monoxide is an unsaturated compound =C=O with two sleeping valencies, p 70 This is in agreement with the ready combination of carbon monoxide with oxygen to form carbon dioxide O=C=O When a mixture of carbon monoxide and sulphur vapour is passed through a moderately hot tube, a gaseous carbonyl sulphide—COS—analogous with carbon dioxide is formed In carbonyl sulphide one atom of sulphur has taken the place of one atom of oxygen in carbon dioxide so that its formula is written S=C=O When CO acts as a radicle, as it appears to do in many reactions, it is called carbonyl Carbon dioxide can thus be regarded as a carbonyl oxide

Carbonyl chloride —Carbon monoxide also directly unites with chlorine in sunlight to form *phosgene*, or carbonyl chloride $COCl_2$ The same gas is produced when a mixture of chlorine and carbon monoxide is passed over bone charcoal (catalytic agent) The gas liquefies at 8° The formation of the gas is conveniently shown by filling two equal-sized gas cylinders, by displacement, one with chlorine, and one with carbon monoxide Place the vessels mouth to mouth and allow the gases to mix thoroughly Both cylinders show the characteristic colour of chlorine Cover each cylinder with a glass plate Let one be exposed to a strong light for a short time, the colour of the chlorine rapidly disappears, and when the glass plate is removed, the contents of the cylinder fume strongly owing to the decomposition of the carbonyl chloride in contact with the moisture of the air The gas also decomposes in contact with water, forming hydrochloric acid and carbon dioxide

$$COCl_2 + 2H_2O = 2HCl + H_2CO_3\text{, and } H_2CO_3 = H_2O + CO_2$$

With an excess of ammonia (NH_3), carbonyl chloride forms urea—$CO(NH_2)_2$ Thus

$$O{=}C\!<\!{}^{Cl}_{Cl} + 4NH_3 = 2NH_4Cl + O{=}C\!<\!{}^{NH_2}_{NH_2}$$

The ammonium chloride—NH_4Cl—is insoluble in alcohol, urea is soluble, hence the two compounds are easily separated.

Metabolic products —Urea is a waste product of animal life Here then, by purely chemical processes, we can build up from the proper elements a compound which is formed by living animals Wöhler's synthesis of urea, by another process, in 1826, appears to have attracted a lot of attention because the teachers of chemistry—Gmelin, Berzelius, etc —then taught that compounds formed by animals and plants were

produced by the action of a vital force, that "within the sphere of living nature, the elements obey laws totally different from those which obtain in inanimate nature," and that "organic substances cannot be prepared artificially" Wohler's synthesis rendered it necessary to reconsider these assertions Wöhler communicated his discovery to Berzelius in these words "I must tell you that I can prepare urea without requiring a kidney or an animal, a man or a dog" Hundreds of different animal and vegetable products have since been prepared in the laboratory, and the hypothesis that a peculiar vital force is necessary for the preparation of these products has been abandoned The growth of the organized structure of animals and plants must not be confused with the formation of chemical compounds

Nickel tetracarbonyl —When carbon monoxide is passed over finely divided metallic nickel[1] at between 40° and 50°, and the gas then passed through a cold tube, a colourless liquid condenses This boils at 43° under a pressure of 751 mm of mercury, and at −25° solidifies to a mass of needle shaped crystals The gas decomposes at 180° into metallic nickel and carbon monoxide The gas burns with a luminous flame, and a deposit of black metallic nickel resembling soot, is obtained when the flame is brought in contact with a cold porcelain dish If the gas be passed through a hot glass tube, dust, or a mirror like deposit of metallic nickel is formed on the glass Mond utilizes this reaction for extracting nickel from its ores Two analyses of the compound furnished 34·26 and 34·33 per cent of nickel These numbers correspond with the formula, $[Ni(CO)_4]_n$ The vapour density of the gas, air = 1, is 6·01, and if hydrogen = 2, 28·75, consequently, the vapour density of nickel carbonyl (hydrogen = 2) is 6·01 × 28·775 = 172·04. The vapour density corresponding with $Ni(CO)_4$ by Avogadro's hypothesis, is 170·68 Hence the formula of nickel carbonyl is written $Ni(CO)_4$ Some consider that the "CO" in nickel carbonyl is a dyad, and the nickel an octad, because of certain physical properties,[2] and write the formula as indicated below, others consider both the nickel and the CO to be dyads

$$\begin{matrix}CO\\CO\end{matrix}\!>\!Ni\!\lessgtr\!\begin{matrix}CO\\CO\end{matrix} \qquad \begin{matrix}C.O\\C\,O\end{matrix}\!>\!Ni\!<\!\begin{matrix}O\,C\\O\,C\end{matrix} \qquad Ni\!<\!\begin{matrix}CO—CO\\CO—CO\end{matrix}$$

Nickel an octad   Nickel a tetrad   Nickel a dyad

As the student acquires familiarity with graphic chemical formulæ, he will find that the arrangement of a number of atoms into a graphic formula, consistent with the valencies of the elements, is sometimes rather a test of man's ingenuity than a representation of the actual grouping of the atoms In some cases, too, it is thought necessary to assume special valencies for particular combinations When it is not possible to decide between several conflicting formulæ, select the most probable, and use the simplest—**hypotheses must not be multiplied without necessity.** This important rule is sometimes called **Occam's razor**

Iron carbonyl —Cobalt does not form a carbonyl under the same

[1] The nickel is best made by reducing nickel oxalate in a current of dry hydrogen at about 300°

[2] Principally the refractive index which is from three to four times as great as is usually exhibited by dyad nickel salts

conditions as nickel[1] If iron be treated like nickel, at 80°, a gas—iron tetracarbonyl, $Fe(CO)_4$—is formed, which burns with a yellow flame The reaction with iron is very much slower than with nickel. At ordinary temperatures the finely divided iron furnishes iron pentacarbonyl—$Fe(CO)_5$—which condenses to an amber-yellow liquid boiling at 103° and freezing at −21° Its vapour density (air = 1) is 6 5 Light decomposes the liquid, forming gold-coloured crystals of iron nonacarbonyl—$Fe_2(CO)_9$ This latter compound decomposes, when heated, forming carbon monoxide, and iron pentacarbonyl. Lamp glasses used for gas burners sometimes appear to redden owing to the deposition of a very thin film of iron oxide on the inner surface, and accordingly it is inferred that a trace of a volatile iron carbonyl is present in the illuminating gas Iron carbonyl is also supposed to be formed in iron cylinders in which "water gas" (p 714) has been stored under pressure for some time

§ 20 Carbon Sulphides.

Molecular weight, $CS_2 = 76\ 14$ Melting point, −110°, boiling point, 46°. Specific gravity of liquid at 0°, 1 292 Vapour density ($H_2 = 2$), 77 06, (air = 1) 2 68

Carbon disulphide was discovered by W A. Lampadius while studying the action of pyrites on carbon Clement and Desormes rediscovered the liquid in 1802 When sulphur vapour is passed over red-hot charcoal, the two elements combine, forming volatile carbon disulphide $C + S_2 = CS_2 - 28\ 7$ Cals This reaction is therefore endothermal, and it bears some analogies with the exothermal reaction $C + O_2 = CO_2 + 96\ 98$ Cals The volatile compound of carbon and sulphur is condensed in vessels surrounded with cold water The product is contaminated with free sulphur, which volatilizes with the carbon disulphide, some hydrogen sulphide is formed at the same time by the action of sulphur on the hydrogen in the charcoal

Manufacture of carbon disulphide —In the manufacturing process, the charcoal is heated in vertical cast iron or earthenware retorts set in a suitable furnace The heat of the furnace also melts the sulphur placed in a vessel near the base of the retort, the sulphur vapour rises through the red-hot charcoal and forms carbon disulphide which escapes at the top The carbon disulphide is condensed in long condensing coils—30 feet long

In Taylor's electric process (1899) a cylindrical furnace 40 feet high and 16 feet in diameter is packed with coke from the top, Fig 242, the coke is renewed through the side hopper *C* An alternating current is sent through the electrodes *E* set at right angles to one another at the base of the furnace The heat melts the sulphur on the floor of the furnace, the vapour of sulphur rises through the coke, forming carbon disulphide Fresh sulphur is introduced through the hopper shown in the diagram The carbon disulphide passes off at the top of the furnace, and is condensed in the condensing coils. The electrical process is practically continuous and is free from troublesome leakages and heat losses incidental to the retort process The crude product can be purified by

[1] This of course does not mean that a cobalt carbonyl cannot be prepared, because $Co_2(CO)_8$ can be made if the reaction occurs under great pressure—150 atmospheres—in the form of orange yellow crystals Colourless crystals of *molybdenum carbonyl*—$Mo(CO)_6$—are known Several other carbonyls are known

repeated redistillation and subsequent agitation with mercury, and distillation from white wax, but the manufacturing process of purification is a "trade secret"

Properties —Carbon disulphide, if pure, is a colourless, mobile, refractive liquid, with an aromatic smell not at all displeasing, although the smell of commercial carbon disulphide is usually disagreeable and rancid. If breathed constantly, in small quantities, it is injurious to health, and in large quantities, fatal Its specific gravity at 0° is 1 292 It freezes at −116°, melts at −110°, and boils at 46° 100 grams of water at 0° dissolve 0 258 gram of carbon disulphide, and at 20°, 0 101 gram It mixes in all proportions with alcohol, ether, benzene, and essential oils It is also a good solvent for sulphur, phosphorus, iodine, bromine, camphor, gums, resins, waxes, fats, and caoutchouc, and it is largely employed in the industries on account of its solvent properties It is also used as an insecticide

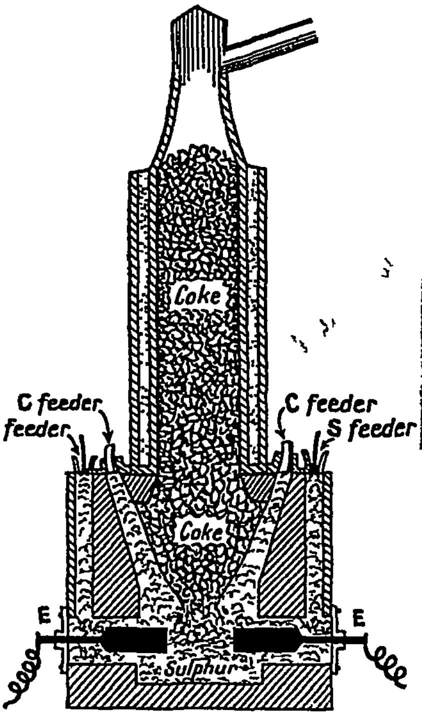


Fig 242 —Taylor's Carbon Disulphide Furnace

Thiocarbonic acid —A compound called thiocarbonic acid H_2CS_3, analogous with carbonic acid, H_2CO_3, is known Thiocarbonic acid is a reddish yellow oil formed by the action of dilute hydrochloric acid on thiocarbonates. It is very unstable, but some of its salts — thiocarbonates — are fairly stable They are formed by the action of carbon disulphide on the sulphides $CS_2 + CaS = CaCS_3$, or on the hydroxides $3Ca(OH)_2 + 3CS_2 = 2CaCS_3 + CaCO_3 + 3H_2O$ Hence CS_2 may be regarded as the anhydride of thiocarbonic acid in the same sense that CO_2 is the anhydride of carbonic acid.

Thiocarbonyl chloride, $CSCl_2$.—If carbon disulphide and chlorine be left in contact for some weeks, particularly if a little iodine be present, a compound, $CSCl_2$, is formed, but the best way of making this substance is to heat a mixture of phosphorus pentachloride and carbon disulphide in a sealed tube at 100° A reaction symbolized $PCl_5 + CS_2 = PSCl_3 + CSCl_2$, seems to occur The compound thiocarbonyl chloride, $CSCl_2$, is related with carbonyl chloride, $COCl_2$ Thiocarbonyl chloride is a fœtid smelling liquid which boils with a little decomposition at 149° The liquid is slightly hydrolyzed by water

Carbon monosulphide, CS —The analogy between the behaviour of sulphur and oxygen in many chemical compounds makes it appear highly

probable that a carbon monosulphide, CS, will exist and will bear the same relation to carbon monoxide, CO, that carbon disulphide bears to carbon dioxide The isolation of carbon monosulphide has proved unexpectedly difficult The reaction between nickel carbonyl and thiocarbonyl chloride furnishes a brown solid which is either carbon monosulphide, CS, or a polymer, C_nS_n The reaction is represented $nCSCl_2 + nNi(CO)_4 = 4nCO + nNiCl_2 + C_nS_n$ The brown product is soluble in concentrated sulphuric acid, and it is precipitated unchanged on dilution Carbon monosulphide is not produced when carbon disulphide acts on nickel carbonyl When electric sparks are passed through the vapour of carbon disulphide at a low pressure, a mixture of carbon monosulphide and unchanged carbon disulphide is obtained The former polymerizes to the brown solid as the temperature rises A bright red liquid carbon subsulphide, C_3S_2, has been made by passing the vapour of carbon disulphide through a quartz tube at 1000° to 1100°, and by exposing the vapour of carbon disulphide to the electric arc The chief interest in this compound turns on its possible analogy with carbon suboxide, C_3O_2

Questions.

1 How many tons of salt and of sulphuric acid containing 70 per cent of real acid are required to make 200 tons of salt cake? Assuming that the manufacturer condenses only 90 per cent of the hydrochloric acid evolved, what weight of this gas is allowed to escape?—*New Zealand Univ*

2 2 4 litres of air at 0° C and 76 cm pressure are shaken with 50 c c of $\frac{1}{100}$ normal $Ba(OH)_2$ solution After removal of the precipitate, the remaining alkali requires 35 c c of $\frac{1}{100}$ normal acid to neutralize it Find the volume of carbonic anhydride in 10,000 volumes of the air —*St Andrews Univ*

3 Give the chief chemical and physical properties of CO_2 and CS_2 —*Owens Coll*

4 Chlorine, sodium carbonate and caustic soda are obtained from common salt Describe fully the chemical reactions involved in the production of these compounds —*Univ North Wales*

5 If hydrogen chloride and carbonic anhydride are found mixed with air and it is desired to separate, one at a time, the substances in the mixture until but one remain, what would be the successive methods employed?—*Amherst Coll, U S A*

6 The absorption coefficient of nitrogen dissolved in water is 0 0152 at 12 6° What volume of the gas measured at standard temperature and pressure is absorbed by one litre of water at 12 6°, at each of the following pressures 1000 mm, 748 2 mm, 391 mm, and 14 3 mm?—*New Zealand Univ*

7 Explain how the qualitative and quantitative composition of carbon dioxide and carbon monoxide have been ascertained —*St Andrews Univ*

8 You are given a mixture of calcium carbonate and calcium sulphate How would you proceed to determine the proportion of each present?—*Aberystwyth Univ*

9 At 20° and 760 mm, a volume of carbonic anhydride is measured and found to occupy 75 litres The gas is passed over red hot carbon and after being brought to the same conditions of temperature and pressure as above, is again measured What volume is the gas found to occupy?—*Amherst Coll, U S A*

10 Apply the law of chemical mass action to the liberation of carbon dioxide from a carbonate by an acid —*Sheffield Scientific School, U S A*

11 How can it be shown that the gas obtained by heating [illegible] is identical with that evolved when marble is acted upon by dilute [illegible] acid? Calculate the volume of carbon dioxide measured at 15° [illegible] pressure obtainable from 10 grams of calcium carbonate (Ca = [illegible] = 12, one litre of hydrogen at N T P weighs 0 09 gram)—*Sheffiel[illegible]*

12 Give a full account of what you learned about [illegible] experiment Contrast sulphites with carbonates, and sul[illegible] dride by carbonic anhydride —*Princeton Univ, U S A*

13 What is meant by the law of mass action? State what you understand by the term "active mass" Discuss from the standpoint of the mass action law (*a*) the dissociation of calcium carbonate by heat, (*b*) the effect produced by adding hydrochloric acid to an aqueous solution of sodium chloride —*St Andrews Univ*

14 The following sentence appears in a modern textbook of chemistry "Men striving to bring individual chemical processes to the highest state of perfection by utilizing all waste products" Illustrate this statement by two examples of the recovery of valuable chemical substances from waste products and explain in detail the chemical reactions involved —*London Univ*

15 Enunciate Gay Lussac's law of gaseous volumes. What change in volume would take place in one litre of oxygen by (*a*) burning sulphur in it, (*b*) converting 6 per cent of it into ozone, (*c*) combining it with twice its volume of carbon monoxide? Accurately describe the way in which you would carry out any one of these experiments —*London Univ*

16 What distinction can be drawn between dissociation and decomposition? Illustrate your answer by reference to calcium carbonate and explain why the presence of free carbon dioxide diminishes the extent to which the dissociation of the substance can proceed at a given temperature —*London Univ*

17 The air of a room was tested for carbon dioxide by drawing 100 litres of it through weighed bulbs, containing caustic potash The temperature was 15° and the pressure 750 mm The increase in weight of the bulb was 0·08 gram What was the percentage by volume of carbon dioxide in the air of the room?—*London Univ*

18 Explain and illustrate the meaning of the expression *coefficient of solubility of a gas* What is meant by the statement that ammonia at ordinary temperatures deviates from Henry's law of solubility?—*London Univ*

19 The acid formed by dissolution of carbon dioxide in water might have its structure represented by the formula $CO(OH)_2$ or $C(OH)_4$ State fully (*a*) the grounds on which the existence of carbonic acid in such a solution may be assumed, and (*b*) the evidence in favour of both these formulæ —*Board of Educ*

20 How are carbonyl, phosphoryl and sulphuryl chlorides respectively prepared? Describe briefly their properties, and show how their characteristic reactions help to elucidate the constitution of the corresponding acids —*Board of Educ*

21 If 12 grams of carbon disulphide were burned in 100 litres of air at 14° and 740 mm, what would be the volume of the gaseous mixture at N T P (*a*) when the combustion was complete and (*b*) when the mixture had been extracted by concentrated caustic potash? How could the relative proportions of the two dioxides be determined? (Air contains 21 per cent of oxygen, and 1 litre of hydrogen at N T P weight 0 09 gram)

22 How do you account for the fact that in spite of the large amount of oxygen consumed in respiration and combustion the percentage of oxygen in the atmosphere remains practically unaltered?—*Victoria Univ, Manchester*

23 What would you observe and what chemical changes (if any) would take place if the following elements were heated strongly in (*a*) a current of air, (*b*) a current of steam —copper mercury, arsenic zinc charcoal?—*London Univ*

24 On passing pure carbon monoxide over copper oxide, it was found that the loss of weight was 24 36 grams and that the amount of carbon dioxide formed was 67 003 grams From these data calculate the atomic weight of carbon (O = 16) How would you make the carbon monoxide required for this experiment, and ascertain its freedom from impurity?—*Board of Educ*

25 What are the common impurities in ordinary water, and to which of them is hardness due? Outline methods by which hardness can be (*a*) reduced, (*b*) removed, and explain why curd is formed when soap is used with hard water —*Sheffield Univ*

26 Describe the principal features of the "mechanical" system of water filtration What is the filter substance in this process, and how is it produced? Give equation?—*Cornell Univ U S.A*

27 How are temporarily hard waters formed in nature? How are they softened? Account for the formation of caves in limestone rock How are the stalactites and stalagmites formed in these caves? What is formed when carbon dioxide gas is passed into a solution of potassium hydroxide? Write all equations —*Princeton Univ U S A*

CHAPTER XXXVI

HYDROCARBONS

§ 1 Methane—Occurrence, Preparation, and Properties

Molecular weight, $CH_4 = 16\ 03$ Melting point, $-184°$, boiling point, $-164°$ Relative vapour density ($H_2 = 2$), 15 95, (air = 1) 0 5547

Occurrence —Methane has been recognized as a distinct compound since 1776 It is often called **marsh gas** because it is often generated in stagnant marshy pools The bubbles of gas which rise to the surface, when the mud at the bottom of a pond is disturbed, often contain methane The gas can be collected in many stagnant ponds by the use of an inverted test-tube full of water and fitted with a funnel as indicated in Fig 243 The funnel directs the bubbles, disturbed by poking a stick into the mud at the bottom of the pond, into the test-tube [1] The test-tube must be securely clamped or it may overturn when full of gas Methane appears to be a product of the gradual decay of vegetable matter in a very limited supply of air This gas is also found absorbed or occluded by coal sometimes under considerable pressure When the pressure is relieved—*e g* when a face of coal is exposed in mining, or during a sudden fall in atmospheric pressure—this gas escapes from coal, sometimes in a continuous stream with a hissing sound—called by the miner a "singer" or a "blower" Methane, mixed with more or less air and carbon dioxide, is common in the atmosphere of coal mines, and hence this gas is found in the air discharged by the "upcast" ventilating shaft On account of its inflammable nature, the mixture of gases occluded in coal is called *firedamp* Other synonymous terms are "light carburetted hydrogen gas" or simply "gas" So far as it is possible to tell by analysis, firedamp (air absent) contains between 80 and 98 per cent of methane, up to 4 per cent of carbon dioxide, and up to 11 per cent of nitrogen Marsh gas and firedamp are therefore more or less impure forms of methane Methane is formed in considerable quantities when coal is heated out of contact with air Coal gas may contain 30 to 40 per cent of methane Enormous quantities of gas, containing 80 to 98 per cent of methane, escape from the petroleum springs in Baku and the Caucasus (Russia), and in the oilfields of Indiana, Ohio,

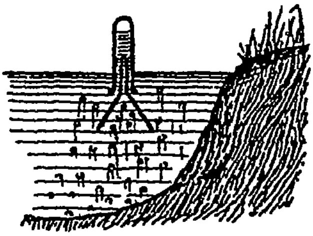


FIG 243 —Marsh Gas

[1] The writer, when a boy, is supposed to have received an attack of typhoid fever as a result of this experiment in a miasmatic swamp

Pennsylvania, etc, where it is called *natural gas*. The percentage composition (volume) of typical samples from Ohio and from Baku is reported as follows

	Hydrogen[1]	Methane	Ethane	Carbon dioxide	Nitrogen	Oxygen
Baku (Russia)	0 9	93 1	3 3	2 2	0 5	0
Ohio (U S A)	1 9	92 8	0 4	0 8	3 8	0 3

Preparation—The gas is usually prepared by the following process Ten grams of fused sodium acetate are intimately mixed with three times that weight of soda lime in a mortar Introduce the dry mixture in a glass or copper flask, or in a copper tube retort Close the copper flask *A*, Fig 244, with a cork to which a delivery tube is attached. The flask is strongly heated, and when all the air is expelled, the methane is collected over water in the usual manner The reaction in the retort or flask is usually represented by the equation $CH_3COONa + NaOH \rightarrow Na_2CO_3 + CH_4$. Soda lime or barium oxide is used in place of sodium hydroxide because of the fusibility of the latter Soda lime is a mixture of calcium hydroxide and sodium hydroxide

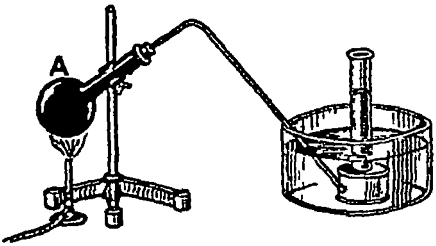


FIG 244 —Preparation of Methane

The gas prepared by this process is not very pure, but the mode of preparation is useful for ordinary purposes For instance, this gas burns with a luminous flame, whereas pure methane burns with a non luminous flame An impure gas—mixed with ammonia and acetylene—is formed by the action of water on commercial aluminium carbide $Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$. When pure methane is required, methyl iodide, CH_3I, is reduced by nascent hydrogen formed by the action of a mercury aluminium couple, or a copper zinc couple on water or alcohol $CH_3I + 2H = CH_4 + HI$ This method of preparation is discussed in works on organic chemistry

Properties—Pure methane is free from colour, and is without smell The gas prepared by the ordinary process usually has a slight smell but this is due to the presence of impurities. Methane is lighter than air 100 volumes of water at 0° dissolve 5½ volumes of the gas, and at 20°, 3½ volumes. Methane is rather more soluble in alcohol It liquefies at 0° under a pressure of 140 atmospheres The liquid boils at −164°, and solidifies at −184° Methane has no well defined physiological action on the system other than diluting the oxygen and so inducing suffocation

Combustion and explosion of methane—When a lighted taper is plunged into a cylinder of this gas, held mouth downwards, the taper is extinguished (non-supporter of combustion), and the gas burns at the mouth of the jar (combustible) The gas, if pure, burns with a pale blue non-luminous flame, forming carbon dioxide and water $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ The gas ignites in air at a temperature between 650° and 750°

[1] Some claim that free hydrogen does not occur in natural gas, and that the alleged presence of hydrogen in these gases is due to a mistake in the analysis That question must be left with the experts in natural gas

If the supply of air be limited, some hydrogen and carbon monoxide will be formed. One volume of methane requires two volumes of oxygen, i e 9 5 volumes of air for complete combustion Such a mixture is violently explosive A red-hot wire will ignite the moist mixture The explosive effect diminishes in violence with increasing proportions of air—a mixture of one volume of methane with 19 volumes of air is explosive, and in the presence of coal dust, W Galloway says that one volume of methane mixed with 111 volumes of air is explosive It must be added that coal dust itself is explosive when mixed with air If a mixture of hydrogen, methane, and air, with an excess of oxygen, be led over palladium-asbestos, the hydrogen alone burns—fractional combustion—the methane is not acted upon provided the temperature of the palladium does not rise above 100° There is no explosion Hence follows a method for estimating the amount of hydrogen in a mixture of hydrogen and methane For the detection of methane, see "Flame caps," p 744.

Action of chlorine —When a mixture of equal volumes of chlorine and methane is exposed to *diffuse daylight*, they gradually react, forming methyl chloride—CH_3Cl Thus $CH_4 + Cl_2 \rightarrow HCl + CH_3Cl$. If more chlorine be present, the chlorine gradually replaces all the hydrogen, forming.

$$CH_3Cl + Cl_2 \rightarrow HCl + CH_2Cl_2 \text{ (dichloromethane)}$$
$$CH_2Cl_2 + Cl_2 \rightarrow HCl + CHCl_3 \text{ (chloroform)}$$
$$CHCl_3 + Cl_2 \rightarrow HCl + CCl_4 \text{ (carbon tetrachloride)}$$

This process of replacing one or more atoms in a molecule by equivalent atoms is called substitution If an excess of chlorine reacts with methane in *direct sunlight* an explosion occurs with the separation of carbon $CH_4 + 2Cl_2 \rightarrow 4HCl + C$ Shake a mixture of one-third volume of methane with two thirds of a volume of chlorine in a gas cylinder, apply a lighted taper Acid fumes of hydrogen chloride will be formed, and soot will be deposited in the cylinder

All the hydrogen can thus be expelled from methane in four stages, and the carbon only in one stage, hence it is probable that the molecule of methane contains one atom of carbon and four atoms of hydrogen Similarly, in dealing with, say, hydrogen chloride (1) only one compound is known, (2) the molecules of hydrogen and chlorine are halved during the formation of two molecules of hydrogen chloride, and (3) the hydrogen and chlorine can only be expelled from hydrogen chloride in one stage Hence it is inferred that the molecule of hydrogen chloride contains one atom of chlorine and one atom of hydrogen, and that each of the molecules of chlorine and hydrogen contain two atoms. This purely chemical evidence agrees with the formulæ based on Avogadro's hypothesis

Composition —If a measured volume of methane be mixed with an excess of air or oxygen, and exploded in a eudiometer, the contraction in volume determines the amount of hydrogen present, since the corresponding amount of water condenses to a liquid whose volume is negligibly small in comparison with the gas The carbon dioxide can be absorbed by potassium hydroxide and the corresponding contraction represents the amount of carbon dioxide formed. In illustration, 10 c c of methane were mixed with 40 c c of oxygen in a Hempel's burette, Fig 189 The mixed gases were driven into the Hempel's explosion pipette, and exploded The gases were returned to the burette, and the volume measured 30 c.c.

instead of the original 50 c c The contraction was therefore 20 c c Water vapour contains its own volume of hydrogen hence 10 volumes of methane contains the equivalent of 20 volumes of hydrogen Again, the gases were transferred from the burette to the absorption pipette charged with potassium hydroxide solution, Fig 231 On returning the gases to the burette, the volume measured 20 c c The contraction due to the absorption of the carbon dioxide was 10 c c, and the 20 c c excess oxygen remained in the burette One volume of carbon dioxide is equivalent to one volume of oxygen and one atom of carbon Hence the analysis has furnished the following data

$$\underset{\text{2 vols.}}{\text{Methane}} + \underset{\text{4 vols}}{2O_2} \rightarrow \underset{\text{2 vols}}{CO_2} + \underset{\text{4 vols.}}{2H_2O_{steam}}$$

or $(CH_4)_n$

The relative density of methane (air = 1) is 0 559, and for hydrogen = 2, we have $28\ 755 \times 0\ 559 = 16\ 07$ If $n = 1$, the vapour density of CH_4 will be $12 + 4 = 16$ Hence the formula for methane is CH_4

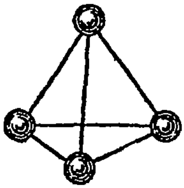
If hydrogen be univalent, the only possible plane graphic formula is

$$\begin{matrix} H \\ H \end{matrix}\!>C<\!\begin{matrix} H \\ H \end{matrix}$$

which makes carbon quadrivalent. Organic chemists can give a number of reasons for assuming that the carbon atom behaves as if it had the form of an equilateral tetrahedron, each apex representing a free valency Thus, if the four valencies of the carbon atom be limited to one plane, it ought to be possible to make the two isomers (*cf* p 650)

$$\begin{matrix} Cl \\ Cl \end{matrix}\!>C<\!\begin{matrix} H \\ H \end{matrix} \qquad\qquad \begin{matrix} H \\ Cl \end{matrix}\!>C<\!\begin{matrix} Cl \\ H \end{matrix}$$

In spite of numerous attempts this has not been accomplished So far as we can tell, all four valencies of carbon are equivalent and symmetrical, or else one of the above compounds is very unstable and, when formed, immediately passes into the stable modification The former hypothesis is much the more probable *The four valencies can only be symmetrical and equivalent if they are directed from a central carbon atom towards the four corners or faces of a regular tetrahedron* The carbon atom thus behaves as if it were shaped like a tetrahedron A graphic representation of the molecule of methane is shown in the adjoining sketch The spheres represent atoms of hydrogen



Methane—CH_4

§ 2 Ethylene—Occurrence, Preparation, and Properties

Molecular weight, C_2H_4 = 28 03 Melting point, −169° boiling point, −103°
Relative vapour density, 28 12 (H_2 = 2) and 0 978 (air = 1)

Occurrence —Ethylene occurs in natural gas (p 692) Some analyses of "pit gases" show that up to 6 per cent of this gas may occur in the air in coal pits, This gas is also obtained when coal or wood is heated in closed vessels and coal gas contains from 4 to 10 per cent of ethylene

Preparation —The gas is most conveniently prepared by the action of dehydrating agents (sulphuric acid, zinc chloride, or phosphoric acid)

upon alcohol—C_2H_5OH. For this purpose put 50 c c of syrupy phosphoric acid in a 250 c c flask furnished with a two-hole rubber stopper fitted with a tap funnel drawn out into a capillary end, and also a thermometer, *T* (Fig 245) The side neck of the flask is connected with a delivery tube leading to an empty wash-bottle, and finally to the gas trough The flask is heated to about 200° on a sand-bath or metal plate. Ethyl alcohol is slowly run from the tap-funnel below the surface of the phosphoric acid The alcohol is decomposed into water and ethylene. The water is retained by the phosphoric acid The reaction is represented in symbols

$$C_2H_5OH \rightarrow H_2O + C_2H_4$$

Other methods of preparation are described in text-books on organic chemistry

Properties.—Ethylene is a colourless gas with a peculiar ethereal odour It has nearly the same density as air 100 volumes of water at 0° dissolve 25 7 volumes of the gas, and at 20°, 15 volumes, the gas is nearly 13 times as soluble in alcohol Ethylene liquefies at 0° under a pressure

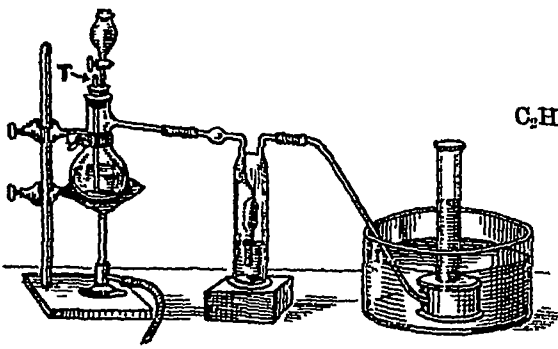


FIG 245—Preparation of Ethylene

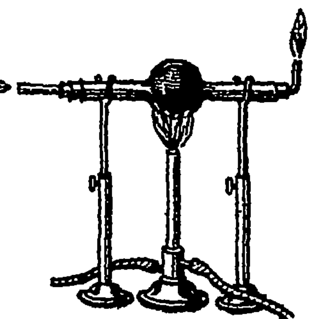


FIG 246 —Decomposition of Ethylene

of 43 atmospheres, the liquid boils at —103°, and solidifies at —169° The gas behaves like methane towards a lighted taper, but it burns with a luminous smoky flame unless it be diluted with hydrogen or methane Ethylene is decomposed at a high temperature This is illustrated by passing the gas through a bulb-tube of hard glass When all the air has been expelled, heat the bulb in the blowpipe flame By rotating the bulb, a mirror-like deposit of carbon can be formed in the interior of the bulb —Fig 246 One volume of the gas requires three volumes of oxygen, or 14 3 volumes of air for complete combustion Such a mixture is a powerful explosive The explosion is more violent than methane

The composition of the gas can be determined by volumetric analysis as in the case of methane The result shows that ethylene is $(C_2H_4)_n$ The vapour density ($H_2 = 2$) is nearly 28 Hence the formula for the gas must be C_2H_4 The graphic formula for ethylene with carbon quadrivalent and hydrogen univalent is not possible if all the valencies have to be saturated or "satisfied." Hence the graphic formula involves two sleeping or unsaturated valencies On joining the carbon atoms by a double bond, we get

$$\begin{matrix}H\\H\end{matrix}\!>C=C<\!\begin{matrix}H\\H\end{matrix}$$

One molecule of ethylene readily combines with chlorine, forming an oily liquid which is ethylene dichloride—$C_2H_4Cl_2$ Half fill a tall cylinder with ethylene, carefully but quickly fill up the cylinder with chlorine, and allow the cylinder to remain in the trough, the water gradually rises in the cylinder, the ethylene dichloride will be seen floating on the surface of the water Hence ethylene was once called *olefiant gas* The oily ethylene dichloride was once termed *Dutch liquid* Similarly with bromine, a litre flask filled with ethylene and 2 c c of bromine will form a colourless oil of $C_2H_4Br_2$, ethylene dibromide, on the bottom of the flask Fill a cylinder one third with ethylene, and two thirds with chlorine Mix the gases well, and apply a light, acid fumes are formed with much soot $C_2H_4 + 2Cl_2 = 4HCl + 2C$. The ethylene molecule also combines directly with sulphuric acid, hydrogen bromide, etc. The compounds of ethylene with chlorine, bromine etc, are called addition products

In gas analysis, ethylene is absorbed in a Hempel's pipette charged with fuming sulphuric acid, or with bromine, and these reagents can be employed to remove ethylene—and *unsaturated hydrocarbons* generally—from a mixture of ethylene, with hydrogen, methane, air, oxygen, and other gases not absorbed by this reagent Methane is not absorbed unless it is left standing in contact with the fuming sulphuric acid for a long time

§ 3 Acetylene—Preparation and Properties

Molecular weight, $C_2H_2 = 26\ 02$ Melting point, $-81\ 5°$, boiling point, $-83\ 6°$ Relative vapour density, $26\ 46$ ($H_2 = 2$), $0\ 92$ (air = 1)

Preparation —M Berthelot prepared it by sparking carbon electrodes in a current of hydrogen gas in a glass bulb as indicated in the diagram —Fig 247 The carbon and hydrogen unite directly $2C + H_2 = C_2H_2$. Pure hydrogen unites directly with carbon at temperatures exceeding 1100° At 1200°, about 0 35 per cent of methane is formed, at 1500°, 0 17 per cent Acetylene, C_2H_2, is also formed at temperatures exceeding 1800° Acetylene is also formed when ethylene is passed through a hot glass tube $3C_2H_4 = 2C_2H_2 + 2CH_4$, and also $C_2H_4 \rightarrow H_2 + C_2H_2$. Acetylene is formed when air burns in coal gas (Fig 284) To show the formation of acetylene when the Bunsen's burner "strikes back" and burns in the metal tube, arrange the apparatus shown in Fig 248. A glass funnel is bent twice

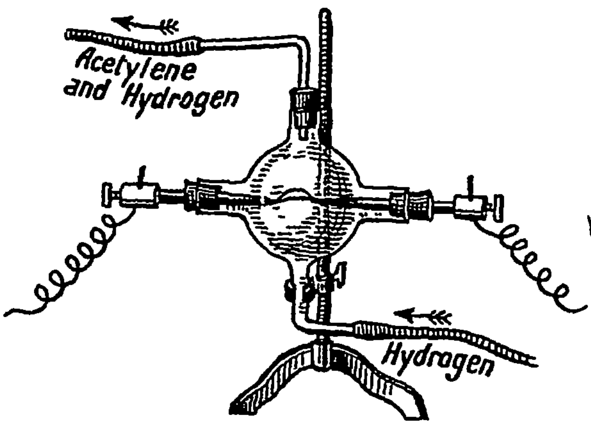


Fig 247 —Berthelot's Synthesis of Acetylene

at right angles and connected with a cylinder containing ammoniacal cuprous chloride.[1] The Bunsen's burner is lighted at the pin-hole jet, and air is slowly aspirated through the apparatus A red precipitate is formed in the cuprous chloride solution. This will be described later The gas is most conveniently prepared by placing fragments of calcium carbide in a dry flask provided with a tap-funnel and delivery tube The delivery tube *C* of Fig 47 can be connected directly with the generating flask at *E*, Fig 249 On gradually admitting water from the tap-funnel, a stream of acetylene is evolved. A modified generating flask is illustrated in Fig 250 In this case the flask is filled with water, and the fragments of calcium carbide are added as required. The reaction between the water and the calcium carbide is represented by the equation $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$ The thermal value of the reaction is 29 1 Cals. The reaction is somewhat complex The "balance-sheet" of the heat concerned in the reaction is usually given as

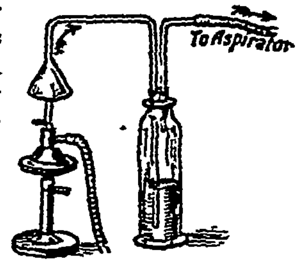


FIG 248 —Acetylene from Coal Gas

Heat liberated	Cals	*Heat absorbed.*	Cals
Formation $Ca(OH)_2$	160 1	Formation acetylene	58 1
		Decomposition of water	69 0
		Decomposition of carbide	3 9
		Balance	29 1
Total	160 1	Total	160 1

The gas contains small traces of sulphur and phosphorus compounds, ammonia, etc , but it is usually pure enough for the experimental work described above The gas can be purified from the most objectionable

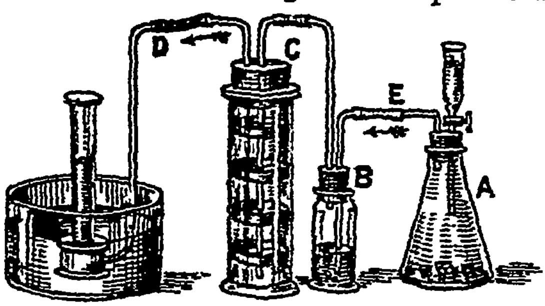


FIG 249 —Preparation of Acetylene

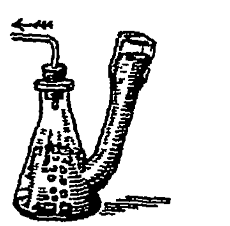


FIG 250 —Rüdorff's Flask.

impurities in the following manner First pass the gas through a wash-bottle containing a solution of copper sulphate acidified with sulphuric acid—*B*, Fig 249 This removes ammonia, phosphorus, and sulphur compounds. The

[1] Ammoniacal cuprous chloride is made by *dissolving 10* grams of cupric oxide with 100 c c of concentrated hydrochloric acid, and the whole boiled for half an hour with an excess of metallic copper Dilute the solution with an excess of water Wash the precipitate twice by decantation with water Dissolve the precipitate in a concentrated solution of *ammonium* chloride If the solution is coloured brown, add a few drops of hydrochloric acid and some strips of metallic copper For use, make the solution *alkaline* with a few drops of ammonia If an acid solution of cuprous chloride is wanted, use hydrochloric acid instead of ammonia

gas then passes through the tower C fitted with perforated shelves on which rest "chloride of lime," this removes the phosphorus compounds This system of purification imitates some industrial plants for the preparation of large quantities of acetylene In Siemens and Halske's process for the manufacture of hydrogen, superheated steam is allowed to act upon calcium carbide so that the formation of acetylene is avoided as much as possible The main reaction is then $CaC_2 + 5H_2O = CaCO_3 + CO_2 + 5H_2$

Acetylene occurs is small quantities among the products of the distillation of coal gas.

Properties —Acetylene is a colourless gas, which, when pure, has an ethereal odour which is not unpleasant As usually prepared and purified the gas has traces of impurities which impart to the gas an offensive smell reminding one of garlic Acetylene is rather lighter than air 100 volumes of water at 0° dissolve 173 volumes of acetylene, and at 20°, 103 volumes of the gas. Alcohol dissolves about six times its own volume at ordinary temperatures. Acetylene is absorbed by fuming sulphuric acid Acetylene is poisonous and soon induces headache The risk of poisoning with acetylene is much less than with carbon monoxide because acetylene is easily detected by its smell The colour of the blood, in cases of acetylene poisoning, is said to be cherry red as with carbon monoxide poisoning, but the hæmoglobin is not affected in the same way There is more hope of recovery with acetylene poisoning than with carbon monoxide poisoning

Action of chlorine —If a gas cylinder be partly filled with acetylene, and chlorine be allowed to pass into the cylinder bubble by bubble, the acetylene flashes as the chlorine enters, and deposits soot on the walls of the cylinder Note that methane and ethylene when mixed with chlorine must be ignited before the soot is deposited This experiment can be varied in an interesting manner by filling a cylinder about one-fifth full with a fresh solution of "chloride of lime," add some hydrochloric acid The cylinder will soon be filled with chlorine gas Add a few pieces of calcium carbide the size of a pea As soon as the acetylene comes in contact with the chlorine, it bursts into flame with the separation of large volumes of soot $C_2H_2 + Cl_2 = 2C + 2HCl$

Combustion —Acetylene burns with a luminous smoky flame, but, like the other hydrocarbon gases, it extinguishes a lighted taper plunged into the gas If acetylene be burned from a jet with a very fine aperture the flame is not smoky, but it is exceedingly luminous In most acetylene burners the gas issues as two small jets so arranged that they strike against one another and produce a flat flame. Other holes are located so that air is drawn in and mixed with the gas as it rushes through the nozzle—*e.g* the gas jet of an ordinary acetylene bicycle lamp The great luminosity of the acetylene flame coupled with the easy preparation of the gas from "carbide," has led to the extensive use of acetylene for bicycle lamps, houses, etc, where coal gas is not convenient, acetylene is also used to increase the luminosity of other inflammable gases If the luminosity (candles per cubic foot) of methane be taken as one unit, the luminosity of ethylene is about 20, and acetylene, about 50 Acetylene is violently explosive when mixed with $2\frac{1}{2}$ times its volume of oxygen The gas cannot be safely stored under a greater pressure than two atmospheres—30 lbs. per square inch—because it is then liable to explode, violently by mere shock. One method of storing acetylene under pressure is to employ a

solution of the gas in acetone, which, under a pressure of 12 atmospheres, dissolves 300 times its volume at ordinary temperatures *Oxy acetylene blowpipes* are used for welding pieces of iron and steel together under conditions where forge welding is impracticable The flame is produced by burning a mixture of the two gases delivered into special blowpipes under pressure (the acetylene from a compressed acetone solution of acetylene) The flame at the apex of the small central white cone has a temperature of about 3000° At that point, the flame is almost entirely carbon monoxide surrounded by a jacket of hydrogen. The temperature at the apex of the flame is too high to allow the hydrogen to combine with the oxygen The flame is therefore hot enough to melt iron and steel, and yet sufficiently reducing to protect the fused metal from oxidation while the welding is in progress The oxy-acetylene blowpipe flame (2400°) is said to be hotter than the flame furnished by any other blowpipe—the oxy-hydrogen flame is about 2000°

Action of heat.—Although stable at comparatively high temperatures —witness its formation in the electric arc (Fig 247)—it is easily decomposed, with the separation of carbon, at lower temperatures For instance when heated in a glass tube to a temperature between 780° and 800° by means of an ordinary gas burner, Fig 246, p 695 The carbon which separates glows brightly owing to the heat developed during the decomposition of the acetylene: $C_2H_2 \rightarrow 2C + H_2 + 50$ Cals. These phenomena (1) ready separation of carbon, and (2) the liberation of thermal energy which raises the temperature of the products of decomposition appear to be related with the high luminosity of the acetylene flame A commercial process for the manufacture of hydrogen is based upon this reaction The separated carbon is employed as a high-grade lamp black If acetylene be passed through a glass tube at a dull red heat, 500° to 600°, and then through a condenser, a few cubic centimetres of an oil will be obtained which, when distilled, furnishes a colourless volatile liquid which boils between 70° and 90° It contains benzene as well as smaller quantities of anthracene, naphthalene, etc Ethylene and methane appear to be formed at the same time The benzene appears to be formed by the polymerization of the acetylene. $3C_2H_2 = C_6H_6$ Acetylene is also decomposed at still lower temperatures, 130° to 250°, in presence of finely divided metals—copper, iron, etc

Acetylides —The amount of acetylene in a mixture of different gases is determined by leading the mixture through an ammoniacal solution of cuprous chloride, when a reddish-brown precipitate of copper acetylide, usually represented by Blochmann's formula, $C_2H_2Cu_2O$, is formed This, when dried, forms copper acetylide, C_2Cu_2, which is *explosive* when heated between 50° and 90°, or subjected to percussion The amount of acetylene is determined by filtering and washing the precipitate with ammoniacal water until the washing water is colourless The precipitate is dissolved in hydrochloric acid, and the copper determined in the usual manner Every gram of copper so obtained represents 0 17 gram of acetylene The presence of acetylene in coal gas can be established by sending a known volume of coal gas through the ammoniacal solution of cuprous chloride An appreciable precipitate is formed in five or ten minutes In the series of hydrogen compounds of nitrogen ranging from ammonia to azoimide or hydrazoic acid, a reduction in the proportion of

hydrogen was attended by increased acidity, so of the carbon compounds, C_2H_6, C_2H_4, C_2H_2, acetylene alone behaves like an acid because its hydrogen atoms can be replaced by a metal The low solubility of acetylene in alkaline solutions shows that its acidic character is probably very feeble

Composition—The composition of acetylene has been established by methods similar to those employed for ethylene and methane The results correspond with the molecule C_2H_2, and the graphic formula H—C≡C—H.

§ 4 Hydrocarbons—Homology

Between 250 and 300 compounds of carbon and hydrogen are known, and they can be arranged in a few series the members of which have many properties in common The first member of each of the following three series is usually treated in inorganic chemistry, and all the series are discussed in organic chemistry

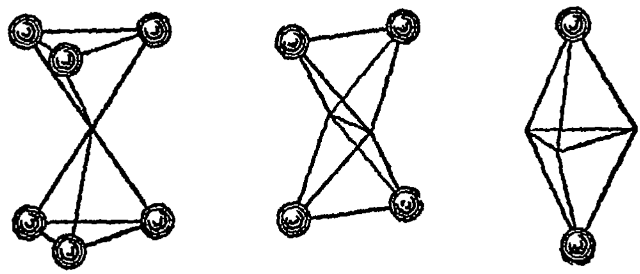
Paraffin Series		Boiling point	Olefine Series		Boiling point	Acetylene Series		Boiling point
Methane	CH_4	−164°	—			—		
Ethane	C_2H_6	−93°	Ethylene	C_2H_4	−105°	Acetylene	C_2H_2	−83 6°
Propane	C_3H_8	−45°	Propylene	C_3H_6	−40°	Allylene	C_3H_4	−23 5°
Butane	C_4H_{10}	1°	Butylene	C_4H_8	1°	Crotonylene	C_4H_6	−27°
Pentane	C_5H_{12}	38°	Amylene	C_5H_{10}	39°	Valerylene	C_5H_8	48°
Hexane	C_6H_{14}	70°	Hexylene	C_6H_{12}	69°	Hexoylene	C_6H_{10}	80°
General formula C_nH_{2n+2}			General formula C_nH_{2n}			General formula C_nH_{2n-2}		

Any member of a series is represented by the general formula of its series As recommended by C Gerhardt (1843), each series is called an **homologous series** because there is a constant difference—CH_2—between any one compound and the next higher or lower member so that all the compounds of the series appear to be proportional In the paraffin series if n be less than five the hydrocarbon is gaseous at ordinary temperatures from $n = 5$ to $n = 15$, liquid, and from $n = 16$ upwards, solid The boiling or melting point usually rises with increasing values of n for each homologous series The hydrocarbons of the first series are rather inert chemically, insoluble in water, and dissolve in one another in all proportions, they are excellent solvents for fats and similar substances, they burn readily, forming carbon dioxide and water, the gases explode when mixed with oxygen and ignited the greater the carbon content the more luminous the flame The terpene series of hydrocarbons—C_nH_{2n-4}—starts with valylene, C_5H_6, and turpentine is the $C_{10}H_{16}$ member The benzene or aromatic series—C_nH_{2n-6}—starts with benzene which is the C_6H_6 member, toluene is C_7H_8, and xylene, C_8H_{10}

Constitution—It is interesting to apply the hypothesis that the carbon atom behaves as if it were a regular tetrahedron to the 2 carbon member of each of the three series indicated above, viz ethane, ethene or ethylene, and ethine or acetylene The diagrams shown on p 701 illustrate how the tetrahedra may be united in each case It has been supposed that the decreasing stability of these compounds with an increase in the number of linking bonds is due to the *bending* and consequent *straining* of the linking bonds from their most stable position—namely, those in which the linking bonds are directed from the centre towards the apices of the tetrahedra

Polymerization—It will be observed that each member of the olefine series might be regarded as an allotropic modification of the other Chemical

analyses show that they all have the *same* percentage composition, and all can be represented by the general formula $(CH_2)_n$. In the case of ethylene, $n = 2$, butylene, $n = 4$, etc. Similarly acetylene—C_2H_2—has the same percentage composition as benzene—C_6H_6. They differ from one another in their molecular weight. Polymerism is a word used to express the fact that two or more different compounds may have the same percentage composition but different molecular weights. Water is probably another example. We are almost certain that in steam most of the molecules are H_2O, in liquid water probably H_8O_4, and in ice the molecule



Ethane—C_2H_6 Ethylene—C_2H_4 Acetylene—C_2H_2

is probably still more complex. The different polymeric modifications of a compound may contain the same elements, but they appear to be associated with different proportions of available energy, *e.g.* $2C + 2H = C_2H_2 - 58.1$ Cals.; $6C + 6H = C_6H_6 - 82.8$ Cals.

The student will have noticed that in naming compounds we usually place the more electropositive element first. Thus, from Table XXIII, hydrogen is more electropositive than oxygen, and accordingly water is said to be a hydrogen oxide, not an oxygen hydride.

§ 5. The Different Kinds of Chemical Action

This is a convenient place to review the different kinds of chemical action so far considered.

I.—Reactions among Molecules of the Same Substance

1. Isomeric changes.—The atoms of the molecule undergo a rearrangement to form a new substance of the same composition as the old, but with different properties, as when ammonium cyanate, NH_4CNO, forms urea, $CO(NH_2)_2$.

2. Polymerization.—Two or more similar molecules may unite together to form a more complex molecule. *E.g.* three molecules of acetylene, C_2H_2, may unite and form one molecule of benzene, C_6H_6.

3. Depolymerization.—A complex molecule decomposes, producing two or more molecules of the same kind, *e.g.* the dissociation of nitrogen tetroxide N_2O_4 into two molecules of NO_2.

4. Condensation.—When two (or more) molecules of a compound unite with the elimination of two (or more) atoms or radicles. *E.g.* when two molecules of sodium sulphite, in the presence of iodine, may each eliminate an atom of sodium, and then unite to form sodium dithionate, and the sodium atoms unite with the iodine to form sodium iodide.

5 Decomposition or analytical reactions —A substance forms two or more different substances *E g* mercuric oxide furnishes mercury and oxygen

II —REACTIONS BETWEEN MOLECULES OF DIFFERENT COMPOUNDS

6 Combination or synthetical reactions —Two or more different substances unite to produce another substance *E g* zinc and oxygen unite to form zinc oxide, calcium oxide and carbon dioxide from calcium carbonate, ethylene and chlorine form ethylene dichloride (addition product)

7 Metathesis or exchange —Two or more substances interact to form two or more new substances Metathesis, from the Greek μετά (meta), beyond, τιθέω (titheo), I place The transposition may involve

(*a*) Simple displacement, replacement, or substitution of one radicle or element for another *E g* metallic iron with copper sulphate forms metallic copper and ferrous sulphate, zinc and hydrochloric acid give zinc chloride and hydrogen.

(*b*) Double decomposition or mutual exchange such as occurs during hydrolysis, neutralization, etc *E g* sodium hydroxide and hydrochloric acid give water and sodium chloride, silver nitrate and sodium chloride gives silver chloride and sodium nitrate

§ 6 Petroleum and Related Products

Occurrence —Crude petroleum—also called *rock oil*—is a thick viscid liquid varying in colour from straw yellow to greenish black, and most varieties show a greenish fluorescence by reflected light Petroleum is a complex mixture of many hydrocarbons belonging principally to the paraffin series along with small quantities of nitrogen and sulphur compounds Petroleum occurs in the Baku district in Russia, in California, Colorado, Indiana, Kansas, Kentucky, New York, Ohio, and Texas in the United States, in Mexico, Canada, India, Egypt, South and West Africa, Peru, Trinidad, Barbadoes, Borneo, Burmah, Australia, New Zealand, etc

The oil apparently occurs underground and in some places it issues from the earth without man's assistance It is usually necessary to "bore" through the overlying strata and insert a pipe in the "oil basin" When first "tapped," the oil often "shoots" out of the "well," but the velocity of the stream gradually subsides,[1] and, after a time, the oil is "pumped" to the surface, conveyed by pipes to a central reservoir for storage, and afterwards distributed Fig 251 is a diagrammatic sketch through the strata of an oilfield, and it is intended to give a rough idea of the way the oil and gas are associated in some oilfields The gas and oil

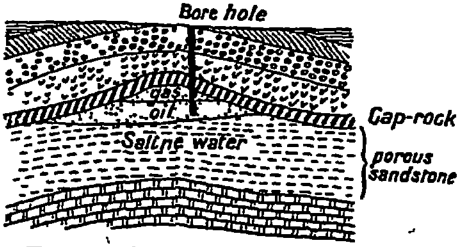


FIG 251 —Geological Section of Oil well (Diagrammatic)

[1] When the Lucas oil well (Beaumont Texas) was first "tapped" in 1901, a six inch stream of oil is said to have spouted 160 feet high for 9 days at the rate of 75,000 barrels per day

here collect near the summit of an anticlinal (concave downwards) fold capped by an impervious rock—called "cap-rock" If the gas is under pressure, it is easy to understand, from Fig 251, how the oil from the "bore" shown in the diagram would be expelled with some violence until the pressure is relieved. Saline water is usually associated with oil and gas In some cases the oil is obtained from a horizontal stratum of porous sandstone or limestone saturated with oil

Origin of petroleum —The origin of petroleum is unknown Some argue that petroleum is a product of the slow distillation of animal or vegetable products—at high or at low temperatures It is assumed in some cases that processes analogous with the manufacture of coal gas are being performed on a colossal scale in the bowels of the earth Others —Mendeléeff, Berthelot—argue that the oils and gas are produced by the interaction of water with metallic carbides—say, iron carbide—at great depths The former view seems to fit most facts better than the latter, although, of course, both theories, and others, may be correct

Refining —Crude petroleum is used as a fuel in many industries—metallurgy, locomotives, fire-engines, steamships, etc A great deal of petroleum is purified or refined. The treatment of petroleum oil and its products is a vast industry Over 200 different commercial products are derived from the purification and refining of petroleum The crude petroleum is placed in a retort—"still"—connected with condensing tubes and receiving tanks The temperature is gradually raised At first, the lighter substances are volatilized and condensed in suitable receivers The receivers are changed when the specific gravity of the distillate has attained a certain value, or when the temperature of the retort has risen sufficiently high The chief fractions are

Table L.—Products of the Distillation of Petroleum

Fraction	Chief contents	Approximate boiling point	Uses
Cymogene	C_4H_{10}	About 0°	Artificial cold
Rhigolene	C_4H_{10} to C_5H_{12}	16°	Local anæsthetic by freezing
Petroleum ether	C_5H_{12} to C_6H_{14}	50–60°	Solvent, fuel.
Gasoline, petrol	C_6H_{14} to C_7H_{16}	70–90°	Solvent, fuel
Ligroïn, naphtha	C_7H_{16} to C_8H_{18}	90–120°	Solvent, fuel
Benzine (not benzene), benzoline	C_8H_{18} to C_9H_{20}	110–140°	Solvent, substitute paint
Kerosene, photogene, paraffin oil	C_9H_{20} to $C_{17}H_{36}$	150–300°	Fuel, illuminant.

The residue in the retort is transferred to another still, and further heated to a high temperature It furnishes lubricating oils, vaseline ($C_{19}H_{40}$ to $C_{21}H_{44}$) used for ointments, etc , paraffin ($C_{21}H_{44}$ to $C_{32}H_{66}$, melting between 45° and 76°) used for candles, insulating, etc The residue in the retort is mainly coke The products may be still further purified For instance, kerosene is washed with sulphuric acid, and then with caustic soda or sodium carbonate and water to get rid of tarry matters and "semi-solid" hydrocarbons which might choke the wicks of lamps, and afterwards

redistilled to remove oils of low flash point (p 741) which might cause an explosion when the oil is used as an illuminant. Sulphur compounds can be removed, to a certain extent, by treatment with cupric oxide The methods for removing sulphur from these oils are mainly trade secrets.

Ozokerite, or ozocerite, is a wax like, dark yellow or brown, native paraffin with a greenish opalescence It is found associated with petroleum in the sandstone of Galicia, where it is extensively mined Small quantities are found in other places Ozokerite when bleached and purified furnishes ceresine—used as a substitute for beeswax, for making ointments, candles, and bottles for storing hydrofluoric acid Ozokerite and asphaltum appear to be residues left after the natural distillation of petroleum Asphaltum or mineral pitch occurs in quantity in the "pitch lake" of Trinidad It may occur as a soft brownish black substance, or as a black solid. It is a mixture of different hydrocarbons and resembles artificial asphaltum or pitch obtained by the distillation of coal tar It is used for making pavements, waterproofing materials, etc

Oil shales —These shales are associated with the sandstones, clays, and limestones of the "calciferous sandstone series" in Mid and West Lothian and other parts of Scotland The oil shales of New South Wales are also called "kerosene shales" Good oil shales can often be lighted with a match, when they burn with a steady flame resembling a candle When heated to dull redness in vertical retorts they furnish gas and a liquid distillate which separates into two layers—the lower aqueous layer contains ammonium compounds, the upper layer has a greenish brown colour and it contains oil and tar This layer closely resembles petroleum and gives similar products on fractional distillation The distillation of oil shales is facilitated by blowing low pressure steam into the retorts Scotch shales furnish from 18 to 50 gallons of crude oil per ton, New South Wales shales are said to yield up to 100 or 150 gallons of crude oil per ton *Dry distillation* or destructive distillation are terms applied to the decomposition of a substance in a closed vessel so as to obtain the volatile products

§ 7 The Calorific Power of Fuels

Thermal energy, heat, is largely employed for domestic and industrial purposes, and a very large proportion of the mechanical and electrical energy employed in the industrial world is really derived from the combustion of carbon in the form of coal In other words, during combustion the chemical energy "stored" up in the fuel is degraded in the form of heat energy, which in turn is transformed into mechanical and also into electrical energy There is unfortunately a tremendous percentage loss in the transformation, and one of the most important problems confronting the chemical engineer is to reduce this loss to a minimum

The commercial value of coal, to a large extent, is determined by its heat of combustion, and consequently, many prefer to purchase coal by a scale based on its heating power, not merely on its price per ton Other things being equal a coal bought at 10s per ton might prove much cheaper than coal at, say, 9s 10*d* per ton, because the heating power, *i e* the available chemical energy, of the former might be greater In commercial work, the amount of heat furnished by the combustion of unit weight (pound, gram, or kilogram) of the fuel is called the calorific power

of the fuel The unit of heat may be the amount of heat required to raise the temperature of one pound of water 1° C—this is called the pound calorie, if 1° F is used, the so-called British thermal unit—B T U—is obtained. Kilogram and gram-calories are also used.

The heat of combustion of carbon (charcoal) is 96,980 cals (p 200) This means that 12 grams of carbon will furnish on combustion to carbon dioxide, 96 980 calories. Hence one gram of carbon will furnish 96 980 ÷ 12 = 8080 cals. This number, 8080 cals., is taken to represent the calorific power of the carbon The calorific power of a few important constituents of fuel are

	calories
Carbon to CO_2	8,080
Carbon to CO	2,400
Carbon monoxide	2,400
Hydrogen (to liquid water)	29,300
Methane, CH_4 (to liquid water)	11,850
Ethylene, C_2H_4 (to liquid water)	10,460
Acetylene, C_2H_2 (to liquid water)	11,500

The calorific power of coal determined in a bomb calorimeter is not very far removed from that calculated from the ultimate composition of the coal on the assumption that the oxygen in the coal will render one-eighth of its own weight of hydrogen useless, so far as the development of heat is concerned

EXAMPLE —A sample of coal furnished, on analysis, 73 per cent of carbon, 6 0 per cent of hydrogen, and 16 per cent of oxygen The other constituents were non-combustibles What is the calculated calorific power of the coal? The analysis means that 1 lb of the coal contains 0·73 lb of carbon, 0 06 lb of hydrogen, and 0 16 lb of oxygen $\frac{1}{8}$ of 0 16 is 0 02, hence, 0 04 lb of hydrogen is available for heating purposes The carbon furnishes 8080 × 0·73 = 5898 4 cals and the hydrogen 0 04 × 29300 = 1172 cals Adding these two results, the calculated calorific power of the coal is 8070 4 cals

The calorific power of gaseous fuels—producer gas water gas, etc—can be determined in a similar manner from the table which precedes There is a small complication in that the analysis of the gases is usually represented by volume The method indicated on p 67 is employed to convert the volumes into weights The calorific power refers to the thermal value of unit weight (pound gram, or kilogram) With gases it is more convenient to express the result as the thermal value of 1000 cubic feet of gas

EXAMPLE —It is required to find the heat of combustion of 1000 c ft of a sample of coal gas which furnished, on analysis hydrogen, 48 per cent, carbon monoxide, 8, methane, 36, ethylene, 3 8, nitrogen, 4 2 per cent

	Percentage composition of gas	Weight of 1 c ft in lbs	Total weight per lb	Percentage weight	Weight per lb of gas
Hydrogen	48 0	0 0056	0·269	8 6	0 086
Carbon monoxide	8 0	0 0871	0 625	20 0	0 200
Methane	36 0	0 0447	1 609	51 4	0 514
Ethylene	3 8	0 0784	0 298	9 5	0 095
Nitrogen	4 2	0 0784	0 329	10 5	0 105
	100 0	—	3 130	100 0	1 000

Thus, 100 c ft of the gas weighs 3 13 lbs

Again,

Combustible constituents	Weight per lb of coal gas	Calorific power per lb	Calorific power, calories
Hydrogen	0.086	29,300	2,517
Carbon monoxide	0.200	2,400	479
Methane	0.514	12,000	6,169
Ethylene	0.095	10,400	990
Total			10,155

1000 c. ft. of the gas weighs 31.3 lbs., and 1 lb. of the gas furnishes 10,155 cals.; consequently, 1000 c. ft. will furnish 10.155 × 31.3 = 317,000 cals.

The student, after solving the problems indicated in what precedes, should have no difficulty in calculating the amount of air required for the combustion; in calculating the composition of the products of combustion; and conversely, as is sometimes needed in industrial work, in calculating the amount of air in excess of that required for complete combustion given the amount of carbon dioxide and oxygen in the flue gases (products of combustion).

§ 8 The Temperature of Combustion

Although the heat of combustion is constant for a definite substance, the actual temperature attained by the combustion is dependent upon a number of factors. One pound of carbon furnishes 8080 (pound) cals. The combustion of one pound of carbon gives $3\frac{2}{3}$ lbs. of carbon dioxide; the specific heat of carbon dioxide is 0.216. From the well known formula: Quantity of heat is equivalent to the mass of substance heated multiplied by the specific heat of the substances heated multiplied by the rise of temperature, we get

$$8080 = 3\tfrac{2}{3} \times 0.216 \times \text{Rise of temperature}$$

Hence the rise of temperature is 10,180°. We have assumed that the carbon was heated in oxygen, and the heat of combustion is spent in raising the temperature of the products of combustion. If the carbon were burnt in air, the $2\frac{2}{3}$ lbs. of oxygen required for the complete combustion of carbon would be accompanied by 8.9 lbs. of nitrogen. If nitrogen be present as well as oxygen, part of the heat will be spent in raising its temperature of the nitrogen. Nitrogen has a specific heat 0.244. Hence

$$8080 = (3\tfrac{2}{3} \times 0.216 + 8.9 \times 0.244) \times \text{Rise of temperature}$$

or the rise of temperature will be 2733°. If an excess of air be present, the temperature will be still further reduced. Hence the calculation of the heat of combustion of a substance requires a knowledge of the composition of the mixture heated, the specific heat of the products of combustion, etc. If the combustion be slow, some of the heat may be lost by conduction, radiation, etc. Then again, the specific heat of gases increases with rising temperatures so that the specific heat of a gas determined at low temperatures, say 100°, is not the same as the specific heat of the gas at, say, 1000°. Hence, calculations of the temperature of combustion, made in ignorance of these factors, are not of much practical value, although they are sometimes useful for purposes of comparison.

EXAMPLE.—*What is the heat of combustion of methane in oxygen and in air when the calorific power is 12,000?* Given the specific heat of steam, 0.480; nitrogen, 0.244; and carbon dioxide, 0.216. Ansr. Nearly 7160° in oxygen, and 2430° in air. Hint: 2.75 lbs. of carbon dioxide, 2.25 lbs. of steam, and 13.4 lbs. of nitrogen are concerned in the combustion of 1 lb. of methane.

§ 9 Gunpowder

If potassium nitrate be mixed with powdered charcoal, and heated, the two materials react with explosive violence, forming potassium carbonate, nitrogen, and carbon dioxide $4KNO_3 + 5C = 2K_2CO_3 + 2N_2 + 3CO_2$ The volume of the gases produced is so much greater than that of the original volume of the mixed solids that if the powder be ignited in a closed space, the expanding gases give the mixture the propelling, tearing, and splitting powers characteristic of explosives. It was soon found that the explosive effect is greater if the nitre and charcoal be mixed with sulphur, so that instead of solid potassium carbonate a residue of solid potassium sulphide is obtained, though side reactions lead to the formation of other products The mixture is called gunpowder Theoretically the reaction is represented: $4KNO_3 + S_2 + 6C = 2K_2S + 2N_2 + 6CO_2$ As an exercise on the methods of calculation indicated on the preceding pages, we can compute the approximate pressure developed during the explosion of gunpowder

Problem.—*To calculate the pressure developed during the explosion of gunpowder in a closed vessel.* For ease in calculation, take the atomic weights C, 12; S, 32; O 16; N, 14; K, 39 It follows that the theoretical mixture will contain 404 grams of potassium nitrate, 64 grams of sulphur, and 72 grams of carbon Otherwise expressed, 75 per cent of nitre, 12 per cent of sulphur, and 13 per cent of charcoal. This very nearly represents the average composition of gunpowder which is usually stated to be nitre, 75; charcoal, 14; sulphur, 10; water, 1 The theoretical equation also shows that 220 grams of potassium sulphide, 56, nitrogen, and 264 of carbon dioxide are formed Otherwise expressed, gun powder on explosion furnishes 59 per cent of gas, or one gram of gunpowder, at 0°, and 760 mm pressure, furnishes 247 3 c c of carbon dioxide and 79 c c of nitrogen, in all, 327 c c of gas consisting of 0 49 gram of carbon dioxide, 0 10 gram of nitrogen, and 0 41 gram of potassium sulphide Again, one gram of an average gunpowder occupies 0 9 c c The surface exposed by one c c is 6 square cm, hence 0 9 c c will expose 5 4 square cm But if 0 9 c c of gunpowder be confined at atmospheric pressure it follows that 327 c c will be confined under 327 — 0 9 = 363 2 atmospheres pressure, or, if one gram of gunpowder at 0° be confined in a closed space and exploded, it furnishes sufficient gas to give 363 2 — 5 4 = 67 3 atmospheres pressure per square cm

The reaction indicated above is exothermal, and much heat is developed The rise of temperature will cause the gas to expand with an ever-increasing pressure One gram of carbon in burning to carbon dioxide develops 8080 cals Hence 0 13 gram of carbon will furnish 1050 cals Assuming that the specific heat, that is the amount of heat required to raise the temperature of one gram of the substance 1°, is constant, and that the specific heat of carbon dioxide is 0 22, of potassium sulphide, 0 4, and of nitrogen, 0 24, remembering also that the quantity of heat Q is equal to the product of the weight of the substance heated, w, the rise of temperature x, and the specific heat s, we have $Q = wsx$, or,

$$1050 = \{(0\ 49 \times 0\ 22) + (0\ 1 \times 0\ 24) + (0\ 41 \times 0\ 4)\}x, \text{ or, } x = 3540°$$

This means that the combustion of one gram of gunpowder will give sufficient heat to raise the temperature of the products of combustion 3540° If 326 c c of gas be heated 3540°, the pressure corresponds with 880 atmospheres per square cm Experiment shows that the observed pressure is but half that indicated by this theoretical discussion The difference is due to several disturbing effects (1) The analysis of the gaseous products of combustion shows that side reactions must also be in progress, for part of the oxygen forms K_2SO_4 some of the carbon burns to carbon monoxide, some of the nitrogen to nitric oxide, some hydrogen and hydrogen sulphide are produced by the decomposition of the water present in gunpowder, and some of the gunpowder remains unburnt, (2) the apparatus in which the test is made is slightly elastic, and this interferes with the accurate measurement of the pressure, and (3) the specific heat of the gas increases appreciably with rise of temperature

§ 10 Coal Gas

When coal is heated in closed vessels to about 400°, it is carbonized and a comparatively small quantity of gaseous, and a relatively large quantity of liquid, products are obtained. The hydrocarbon gases consist mainly of members of the methane and ethylene series. Benzene, acetylene, and hydrogen are generally present. If the temperature of distillation be raised, the quantity of liquid products decrease, and the quantity of gaseous products increase. In other words, more gas and less tar is obtained. The gas obtained by the high temperature distillation has less illuminating power. This is illustrated by the following table.

TABLE LI.—EFFECT OF TEMPERATURE OF FORMATION ON THE ILLUMINATING POWER OF COAL GAS

Approximate temperature	Volume of gas c. ft.	Illuminating power—candles
420°	1 400	—
700°	6 250	20 5
900°	9 090	17 8
1000°	10 820	16 7
1200°	12 000	15 6

This decrease in the illuminating power is due to the decomposition of the hydrocarbons into simpler compounds—hydrogen and gas carbon. The illuminating power of the gas depends upon the proportion of "total hydrocarbons" present, and not on any single one. In modern practice there is a tendency to raise the temperature of distillation, thus sacrificing quality (*i.e.* illuminating power) for quantity (*i.e.* cubic feet per ton of coal). The gas varies in composition with the nature of the coal, the temperature of decomposition, etc. The tar, carbon dioxide, sulphur and ammonia compounds, etc.—produced during the distillation of the coal—are removed from the gas, and finally, when the distillation is conducted in the neighbourhood of 1000°, purified coal gas contains approximately

Hydrogen	Methane	Ethylene	Carbon monoxide	Carbon dioxide	Nitrogen	Oxygen	
49	35	4	4	$\frac{1}{2}$	4	$\frac{1}{2}$	per cent

The approximate proportions of the by-products produced at the same time, are, per ton of coal

	lbs	per cent
Coal gas (10,000 c. ft.)	380	17 0
Tar	115	5 1
Gas liquor (without water from scrubbers)	177	7 9
Coke	1568	70 0

There are differences in detail in the manufacture at different gasworks. The following brief description assisted by the diagrammatic sketch, Fig. 252, will give a rough idea of the process of manufacture.

1. The retorts.—The coal is distilled in D shaped fireclay retorts 6 to 8 feet long. The retort may be set horizontally, vertically, or slanting. On small works, the retorts are closed at one end, and in larger works, open at both ends. The retort is fixed to the iron furnace front

which is provided with a door, and connected with a vertical exit pipe—the *ascension pipe*—for the escape of the volatile products The retorts are generally arranged in tiers of 5, 7, or 9, so that they can be heated by a single furnace The charge—about 200 lbs. of coal—is distributed evenly over the bottom of each retort and the mouth of the retort luted air-tight The retorts are heated by the furnace which will be discussed later The volatile products pass from the retort into the *hydraulic main* which contains condensed coal tar and water This main runs horizontally over the front of the bench of retorts, and all the retorts discharge into it The gas is here partly cooled, and some tar and water are condensed from the hot gas. The pipe leading the gas from the retort dips into the liquid in the hydraulic main, and so prevents the gas from passing back—" back lash "—when the retorts are recharged The liquid in the hydraulic main is kept at a constant level by leading any

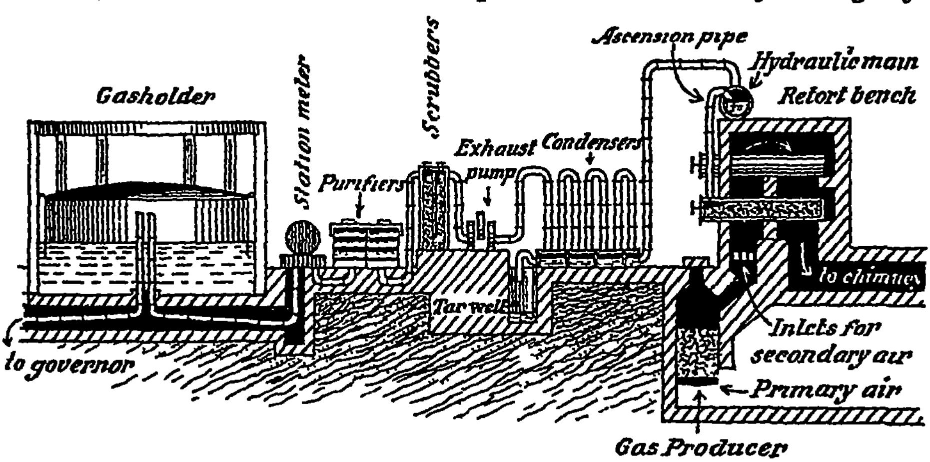


FIG 252 —Coal Gas Works (Diagrammatic Section)

excess into the *tar well* In from four to six hours, the distillation will be complete The coke is pushed or raked from the retort, and quenched with water to prevent further combustion Another charge of coal is quickly introduced into the retort The residual coke may be used for heating the retorts, and part is sold

2 The condensers —The hot impure gases pass from the hydraulic main into a series of iron pipes, several hundred feet long—the condensers—connected so that the gas must pass through the entire length of the pipe The gas is here cooled still further, and more tar is condensed and run to the tar well The condensed liquid in the tar well separates into two layers—the lower layer is *gas tar*, and the upper aqueous solution containing ammonia and ammonium salts is the *gas liquor* The gas is drawn from the hydraulic main through the condensers by means of an *exhaust pump* which reduces the pressure in the retort, and also regulates the pressure of the gas sent along to be still further purified

3 The scrubbers —In modern works all the tar is removed from the gas in the condensing plant, but the gas still contains sulphur compounds, carbon dioxide, some ammonia, and possibly some tar In one form of scrubber, a tower is filled with trays charged with coke or pebbles The tower has a partition so that the gas flows down one side of the tower

and up the other A spray of water trickles down the coke The gas in passing through the coke is broken up into small bubbles and washed free from ammonium compounds by the water The water is drawn off intermittently at the base of the tower and mixed with the gas liquor from the tar well The ammonia is recovered as a by product

4 The purifiers —Some of the hydrogen sulphide and carbon dioxide in the gas combine with the ammonia and are removed in the scrubbers. The gas still contains sulphur compounds If these were not removed, the burning gas would form sulphur dioxide[1] which is objectionable The object of the purification is to remove the sulphur compounds and the carbon dioxide The gas leaving the scrubbers is directed into a series of low rectangular iron tanks—the purifiers—fitted with horizontal shelves or grids The shelves are loosely packed with a layer of slightly damped slaked lime—say, six inches deep The lime removes hydrogen sulphide and carbon dioxide A mixture of calcium sulphide—CaSH OH, or $Ca(SH)_2$—and calcium carbonate is formed The calcium sulphide may absorb some carbon disulphide

$$2Ca{<}^{SH}_{OH} + CS_2 = Ca(OH)_2CaCS_3 + H_2S$$

When the lime is spent or fouled it is called *gas lime*, or *spent lime* To make sure that all the sulphur compounds are removed, the gas is generally passed through another purifier containing ferric hydroxide ("bog iron ore")—$Fe_2O_3\,H_2O$ The ferric hydroxide forms ferric sulphide $Fe_2O_3H_2O + 3H_2S = Fe_2S_3 + 4H_2O$, or ferrous sulphide and free sulphur $Fe_2O_3H_2O + 3H_2S = 2FeS + S + 4H_2O$

When the mixture is fouled it is placed in a heap for about twenty four hours,[2] and then spread out in layers twelve inches deep The layers are turned over repeatedly to expose fresh surfaces to the action of the air The black iron sulphides are oxidized by exposure to the air, and free sulphur separate $2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6S$, $4FeS + 3O_2 = 2Fe_2O_3 + 4S$, the net result is that the hydrogen sulphide of the gas is converted into free sulphur, and the ferric oxide is revived ready to be used again This alternate fouling and oxidizing of the "iron" is repeated about sixteen times when so much sulphur accumulates—55 per cent —that it is no longer economical to use the oxide again The *spent oxide* is sold to the manufacturer of sulphuric acid, and used as a source of sulphur

5 The gas holder —The purified gas next passes through a large meter—*station meter*—which records its volume The gas holder is an enormous cylindrical iron tank which floats in a cistern of water, and rises or falls as gas enters or leaves The cylinder is so weighted that the gas can be expelled from it at the necessary pressure From the gas holder, the gas passes to the *governor*, where its pressure is reduced and regulated so as to give a supply of gas at the necessary pressure.

6 The by-products.—(1) *Coke* is a valuable fuel and finds a ready sale (2) *Gas carbon* is a hard dense deposit of almost pure carbon which

[1] There is no experimental evidence to show that the sulphur forms sulphuric acid in a moist atmosphere unless the temperature be so low that the water is condensed to a liquid (*cf* p 418)

[2] When fouled for the first time the mixture may absorb oxygen so rapidly that the rise of temperature may destroy the wooden grids in the purifier Some prefer to use a mixture of old and new ferric oxide so as to lessen the risk of ignition

gradually collects on the inside of the retort It is a good conductor of electricity, and is used for the manufacture of carbon rods for electric lighting, and of plates for galvanic batteries (3) *Gas lime* is used for agricultural purposes (4) *Tar*—gas tar, coal tar—is a black viscid foul-smelling liquid used as a protective paint for preserving timber, making tarred paper, waterproofing masonry, etc Tar is a mixture of many "organic substances" which are separated by distillation at different temperatures. It furnishes carbolic and creosotic oils, benzene, naphthalene, anthracene, dyestuffs, flavours, perfumes, oils, etc The residue in the retort is "pitch" Asphalt is a solution of pitch in heavy tar oils, and is used in making hard pavements, varnish, etc (5) *Ammonia* The ammoniacal liquid is boiled with milk of lime and the expelled ammonia is mixed with sulphuric acid. The tarry matters are separated, and the solution of ammonium sulphate is evaporated and crystallized for the market

§ 11 Producer Gas

We have seen that carbon can unite directly with two different proportions of oxygen forming carbon monoxide and carbon dioxide The former, carbon monoxide, can be conveniently regarded as *partially burnt* carbon, and the latter, carbon dioxide, as the final product of the combustion One pound of carbon burning to carbon monoxide will furnish 2400 cals, and the resulting carbon monoxide will generate 5680 cals. on combustion Thus, one pound of carbon will produce

	$C \rightarrow$	$CO \rightarrow$	CO_2
Weight	$1 \rightarrow$	$2\frac{1}{3} \rightarrow$	$3\frac{2}{3}$ pounds
Heat	$\rightarrow$	$2400 \rightarrow$	$5680 =$ total 8080 cals

In furnaces designed to make "fuel gas" by the partial oxidation of coke, the products of the actual combustion of the coke pass through a deep bed of hot fuel Carbon monoxide is the result The carbon monoxide can be led to any desired spot and burnt to carbon dioxide The furnace is called a *producer* or generator,[1] and the gas coke producer gas, or coke generator gas. The *solid* coke in the producer is partially oxidized so as to furnish a *gaseous* fuel —hence the term fuel gas is sometimes used for gaseous fuels The idea was first put into practice by C Bischof in 1839 The modern producer is a modification of Bischof's original producer in some minor details In Fig 253, *A*, is the charging hopper of the producer The hopper is filled with fuel, the upper lid placed in position, the lower shelf is drawn to the side so that the fuel drops into the producer without allowing the gas to escape *B* represents the firebars, *C* the exit flue for the passage of the products of the partial

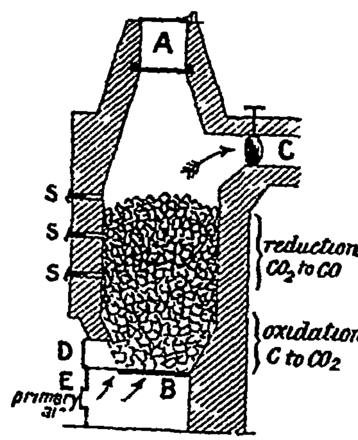


FIG 253 —Bischof's Producer (1839)

[1] For other producers, see Figs 234 and 252

combustion of the carbon, D is a door for cleaning firebars, etc, when required, E regulates the amount of—so called—primary air admitted to the firebars S represents "spy holes" for poking, etc The shape of the producer shows that it has been modelled after the blast furnace where a combustible gas is obtained as a by-product in the smelting of iron Instead of depending upon the blast furnace for gaseous fuel, Bischof apparently conceived the idea of making a similar furnace to supply nothing but gaseous fuel

Since every volume of oxygen in air is accompanied by four volumes of nitrogen, coke producer gas, obviously, must contain both carbon monoxide and nitrogen Under ideal conditions, it follows that coke producer gas contains

	Volume	Weight
Carbon monoxide	34 7	34 7
Nitrogen	65 3	65 3

But one pound of carbon, burning to carbon dioxide, develops 2400 units of heat. Hence 0 347 lb of carbon monoxide, or 1 lb of producer gas will develop 846 units of heat This number represents the calorific

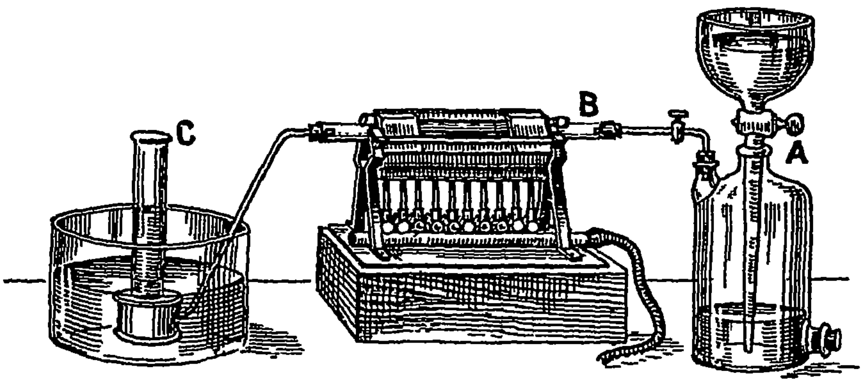


FIG 254 —Preparation of Producer Gas

power of coke producer gas. But one pound of carbon produces 6 7 lbs. of coke producer gas. Hence

Heat from 1 lb of carbon	8080 cals
Heat of 6 7 lbs coke producer gas	5665 cals
Heat lost in conversion	2415 cals

Hence, about 30 per cent. of the heating value of the coke is lost by the conversion of the solid coke fuel into gaseous coke producer gas This loss is represented by the heat generated in the producer itself while burning the coke to carbon dioxide Industrially this loss must be counterbalanced in some way, or the use of the coke producer gas will be less efficient than direct firing with solid fuel

Reactions in the producer —The reactions in the producer can be imitated on a small scale in the laboratory If a hard glass or porcelain tube B be packed with charcoal, and connected at one end with a gas holder containing air, A, Fig 254, and the other end with a delivery tube and gas trough, C, when air is slowly driven through the bed of hot

charcoal, carbon monoxide mixed with atmospheric nitrogen collects in the gas jar. The gas burns with a blue flame It is coke producer gas.

Attempts to find if carbon burns first to carbon dioxide or to carbon monoxide have not given any decisive result In every case both gases have been detected among the products of the reaction. Hence it is not at all unlikely that we are dealing with concurrent reactions typified by decomposing potassium chlorate (p 137) ·

$$3C + 2O_2 \begin{array}{l} \nearrow 2CO \\ \searrow CO_2 \end{array}$$

The relative proportions of carbon monoxide and carbon dioxide formed during the action are determined by the temperature There is also an interaction between the excess of carbon and the higher oxidation product since the reaction $CO_2 + C \rightleftharpoons 2CO$ is a balanced reaction The relative proportion of carbon dioxide to carbon monoxide, for equilibrium, is here again determined by the temperature For instance, any mixture of carbon monoxide and carbon dioxide when heated in the presence of carbon produces at.

Temperature	Per cent by volume	
	CO	CO_2
450°	2	98
750°	76	24
1050°	99 6	0 4

This also shows that if the temperature of a producer be in the vicinity of 450° very little combustible gas will be obtained, and conversely, in the vicinity of 1000°, nearly the maximum possible amount of combustible carbon monoxide will be present. Hence the temperature of the producer should be about 1000° in order to get the maximum yield of carbon monoxide with a minimum loss of heat

In the combustion of gaseous carbon compounds, the carbon appears to burn first to carbon monoxide (p 752) Highly purified carbon may be heated to redness in well-dried oxygen without producing the characteristic glow of carbon in oxygen, while but a very small amount of carbon dioxide and a large amount of carbon monoxide are obtained. There is nothing to show that the mechanism of the reaction with perfectly dried materials as in Baker's experiment is the same as when moisture is present

Coal producer gas—If coal be used in the producer in place of coke the coal near the top of the fuel bed will be distilled, and form coal gas. The resulting ' fuel gas ' will therefore be a mixture of coal gas and coke producer gas. But coal gas, as indicated on p 705, has a relatively high calorific power, viz. 10 155 cals. Hence, the use of coal in place of coke will raise the calorific power of the producer gas. The loss in the percentage of available heat will not be so great because part of the heat is utilized in distilling the coal. One advantage of using coal producer gas arises from the fact that slack, and inferior coal generally, can be employed under conditions where a more expensive coal would be needed for direct firing

Burning producer gas—The chemical engineer is constantly confronted with the "fuel problem" and in some works the composition of the producer gas and of the flue gases is regularly tested to ensure efficient working Constructional details, type of burner, type of flame, etc, have also to be carefully studied. It is obvious that if the flue gases leave the furnace

hot, and the hot gases are allowed to escape into the air, a certain percentage of heat is wasted There are several systems for utilizing this heat to warm up the air required for the combustion of the fuel gas, etc It will be noticed that in burning solid fuel partly in the producer, and finally in the furnace, two separate supplies of air are needed. The first supply, used for gasifying the fuel, is, for convenience, called the primary air, and the second supply used for burning the gaseous fuel in the furnace is conveniently styled the secondary air See Fig 252, p 709

The blue lambent flame which sometimes flickers over a *clear* coke (or coal) fire is burning producer gas The air—primary air—entering at the grate reacts with the red hot carbon $C + O_2 = CO_2$, and this passing through the red hot carbon of the fire is reduced $CO_2 + C = 2CO$ The carbon monoxide on top of the fire meeting air—secondary air—burns to carbon dioxide with a blue flickering flame $2CO + O_2 = 2CO_2$.

§ 12 Water Gas

When carbon is heated in a gas producer, and a current of steam is blown through, the two interact forming hydrogen and carbon monoxide —both combustible gases $C + H_2O \rightleftharpoons CO + H_2$. The resulting mixture has a very high calorific power It is called water gas. Water gas is almost free from diluting nitrogen If the reaction occurs below 1000°, carbon dioxide begins to accumulate in the gas, and thus the more the lower the temperature of the reaction. For instance, Bunte found

TABLE LII —EFFECT OF TEMPERATURE OF FORMATION ON THE COMPOSITION OF WATER GAS

Temperature	Per cent of steam decomposed	Percentage composition of gas produced		
		Hydrogen	Carbon monoxide	Carbon dioxide
674°	8 8	65 2	4 9	29 8
1010°	94 0	48 8	49 7	1 5
1125°	99 4	50 9	48 5	0 6

For convenience in thinking, let us suppose that the reaction occurs in two stages (1) decomposition of the water $2H_2O = 2H_2 + O_2$, and (2) oxidation of the carbon by the liberation of oxygen $2C + O_2 = 2CO$ The heat required to decompose the water in the first reaction is greater than the heat given off during the combustion of the carbon by the liberated oxygen Thus

Heat absorbed in decomposing 18 lbs steam	−58,600 cals
Heat evolved in burning 12 lbs of carbon to CO	+29,520 cals
Heat absorbed during the reaction	−29,080 cals

Hence the producer must be getting cooler all the time the steam is passing through the fuel bed. It appears to be necessary to provide heat from an outside source to maintain the temperature of the producer sufficiently high to prevent undue amounts of carbon dioxide accumulating in the products of the reaction It is not economical to heat the producer

externally, and make the formation of water gas continuous. In modern water gas plants, the carbon in the producer is raised to incandescence by a blast of air—the *air blow*—continued for about ten minutes. This is followed by a jet of steam until the temperature falls to dull redness—*steam blow*—continued for about four minutes. When the air blow is in progress, the producer is not making water gas, and in consequence, a damper is used to deflect the stream of gas from the producer elsewhere.

The water gas reaction can be illustrated by substituting a flask in which water is boiling for the gas holder, *A*, Fig. 254. The gas which is collected can be analyzed by mixing a definite volume with air in Hempel's burette (p. 523), and exploding it in Hempel's pipette. Note the diminution in volume, and then absorb the carbon dioxide as indicated on p. 661. The data so obtained enable the amount of hydrogen and carbon monoxide to be calculated.

Semi-water gas.—By combining the operations for making producer gas and water gas—mixing the air which passes through the producer with just sufficient steam to maintain the temperature of the producer—the extra heat developed during the oxidation of carbon to carbon monoxide is utilized in decomposing the water vapour. In practice, it is found that at least 4 lbs. of carbon should be burnt by the air for every 1 lb. of carbon "burnt" by the steam. Under these conditions, the gas from a producer burning coke will be a mixture of water gas and coke producer gas. Under ideal conditions therefore we should have a gas containing carbon monoxide, 37.0; hydrogen, 7.4; and nitrogen, 55.6 per cent.; and possessing a calorific power of 1144 cals. as opposed to 846 cals. with simple coke producer gas where steam is not used. Consequently, instead of losing 30 per cent. of the heat value of the fuel in the conversion, only 20 per cent. is lost.

In modern producers, the fuel gas is made by blowing steam and air into the body of the producer fed with slack coal. The result is a mixed producer gas, also called semi-water gas. For the sake of comparison, analyses of coke and coal producer gases, water gas, mixed coal producer gas, and carburetted water gas are indicated in Table LIII.

TABLE LIII.—PERCENTAGE COMPOSITION OF FUEL GASES BY VOLUME

	Constituent	Coke producer gas	Coal producer gas	Water gas	Mixed coal producer gas	Carburetted water gas
Combustible	Methane	0.8[1]	2.0	1.3	1.2	16.8
	Ethylene	0.0	0.4	0.0	0.2	8.7
	Carbon monoxide	32.3	24.4	45.6	25.2	28.7
	Hydrogen	4.0[2]	8.6	46.3	18.2	40.2
Non combustible	Nitrogen	61.2	59.3	4.2	49.1	4.3
	Carbon dioxide	1.6	5.2	2.1	6.0	1.2
	Oxygen	0.1	0.1	0.1	0.1	0.1
Calorific power (approx.)		890	1130	3560	1320	6060

[1] Derived from the hydrocarbons remaining in the coke.
[2] Derived from the moisture in the fuel and in the air.

The calorific powers of these gases may be compared with 10,155 cals obtained for coal gas, pp 705–6

§ 13 Enriched or Carburetted Water Gas

Water gas burns with a non luminous flame, and, though a valuable heating agent, it is useless for lighting purposes unless it be employed in conjunction with, say, a Welsbach's mantle Hence, if water gas is to be used as an illuminating agent, it is charged with hydrocarbon gases which do not condense on cooling The mixture is called carburetted or enriched water gas. The carburetting is conducted as follows When the air blast is in progress, the products of combustion from the top of the producer are deflected down a tower containing checkered brickwork, and called the *carburetter*, then up another tower also containing checkered brickwork, called the *superheater*, and thence into the air The result of this is to raise the temperature of both towers—the carburetter and the superheater The air valve at the top of the superheater is deflected so that the superheater is put in communication with a third tower resembling the *scrubber* of a gas works. A spray of oil is simultaneously directed into the top of the carburetter, and steam is blown into the producer As the water gas and oil pass down the hot carburetter, the oil is decomposed—"cracked"—and the decomposition is completed in the superheater In this way, the oil is transformed into gases which do not liquefy when cooled. The gas is purified and washed in the scrubber, and thence passed to the gas holder

A gas called illuminating gas, and sometimes, by courtesy, "coal gas," is a mixture of 50 to 70 per cent of carburetted water gas with coal gas The high percentage of carbon monoxide makes such a gas far more poisonous than coal gas In the so called *Pintsch's oil gas,* the oil is sprayed into hot retorts and then passed through a condenser, scrubber, and lime purifier into the gas holder

Questions

1 What are hydrocarbons? What is a homologous series? When a hydrocarbon burns in the presence of an excess of air what are the products of combustion? How is ethylene prepared? Give the equation representing the change which takes place when ethylene burns in air What is formed when ethylene is mixed with an equal volume of chlorine? Give the equation —*Princeton Univ U S A*

2 How is coal gas manufactured and purified? What are the by products? Name the diluents the illuminants, and the impurities present in ordinary coal gas —*Princeton Univ, U S A*

3 A sample of coal contains 84 per cent of available carbon, and 6 per cent of available hydrogen What weight of atmospheric air will be required to burn 1 cwt of the coal?—*Coll of Preceptors*

4 How may it be proved that any given volume of ethylene (olefiant gas) contains twice as much carbon as an equal volume of marsh gas but the same amount of hydrogen?—*London Univ*

5 100 c c of a mixture of CO and CS_2 vapour were mixed with 300 c c of oxygen and fired After cooling, the resulting gases occupied 340 c c and after absorption by potash 200 c c of oxygen remained Show how the composition of the mixture may be determined by *each* of the following data (i) the contraction, (ii) the absorption, and (iii) the oxygen consumed —*Victoria Univ, Manchester*

6 About what proportion of the total heat given out on the complete com

bustion of carbon is sacrificed by first converting the carbon into carbon monoxide? Give any explanation you can of the probable causes of this difference What do you understand by the expressions "endothermic" and "exothermic" compounds?—*London Univ*

7 Explain as fully as you can the statement that "ethylene dibromide may be regarded either as an additive compound of ethylene, or as a substitution derivative of ethane"—*London Univ*

8 What is meant by "saturated" and "unsaturated" compounds? Illustrate your answer by taking as examples carbon monoxide, carbon dioxide, marsh gas, and ethylene—*London Univ*

9 What is meant by the expression—"a homologous series"? Give an instance of such a series, with names and formulæ—*London Univ*

10 Calculate the heat of formation of methane, CH_4, given —$C + O_2 = CO_2 + 96\ 9$ cals, $H_2 + O = H_2O + 68\ 4$ cals, and $CH_4 + 4O = CO_2 + 2H_2O + 213\ 5$ cals—*French Coll*

11 10 c c of a gaseous hydrocarbon are exploded with an excess of oxygen. A contraction of 15 c c is observed After the explosion, a further contraction of 20 c c is observed on treating the resulting gases with potassium hydroxide solution What is the molecular formula of the hydrocarbon?—*Customs and Excise*

12 18 c c of a gas, when mixed with 18 c c of oxygen, and exploded, contracted to 15 c c On adding potash, a further contraction of 6 c c took place, and the residual gas was entirely absorbed on the addition of pyrogallol The vapour density of the gas was found to be 5 33 c c and none of it was capable of absorption by potash before the explosion Draw any conclusions you can as to the nature of the gas, and state by what experiments you would seek to confirm them.—*Oxford Univ*

CHAPTER XXXVII

ALLOTROPIC FORMS OF CARBON

§ 1 Amorphous Carbon—Lampblack.

IT remains to discuss the properties of the allotropic forms of carbon

1 The term "amorphous carbon" is used to include the different varieties of vegetable and animal charcoals—lampblack, charcoal, soot, gas carbon (p 710), and coal These are non crystalline more or less impure forms of carbon The term "amorphous," however, is rather carelessly used Strictly speaking, the word is synonymous with "non crystalline," but it is sometimes used in reference to the mere external irregular shape of the granules rather than to the internal crystalline structure (p 177)

2 Graphite includes the so called amorphous and crystalline graphite

3 Diamond includes boart and carbonado

That these are different forms of the one element is proved by the experiment indicated on p 658 Pure varieties of each form—sugar char coal, graphite, and diamond—furnish on combustion the same amount of carbon dioxide per gram of material, although the heat evolved during the combustion of twelve kilograms of each form is different Other characters also vary, *e g*

	Diamond	Graphite	Charcoal
Heat of combustion (Cals)	94 31	94 81	97 65
Specific gravity	3 5	2 5	1 6
Specific heat	0 1469	0 2017	0 2415
Ignition temperature (oxygen)	800°–875°	650°–770°	300°–500°

These are therefore different forms of one element associated with different amounts of available energy

A comparison of the atomic weights of carbon, nitrogen, and oxygen, and the large number of volatile compounds formed by carbon might make it probable that its molecule is C_2 The high boiling and freezing points, and the chemical inertness of carbon, on the other hand, make it appear as if the molecule is complex and a comparison of the results in the above table has led to the assumption that the molecule of carbon in the diamond is more complex than in graphite, and in graphite more complex than in charcoal

Lampblack is made by burning substances rich in carbon in a limited supply of air so that the maximum amount of smoke is developed—for example, turpentine, petroleum, tar, acetylene, etc The smoke is passed into large chambers in which coarse "blankets" are suspended The "soot" collects on the blankets Lampblack is also made from natural gas A ring of burners is mounted below a cast iron disc with a groove on the rim convex downwards in such a way that the flame from each burner is divided into two parts Cold water runs into the upper side of the groove, and away *viâ* the hollow shaft which rotates the iron disc This keeps the metal in contact with the burning coal gas. Soot is deposited on the groove As the disc revolves, an automatic scraper removes the lampblack from the grooves of the disc The lampblack falls into a hopper and is conveyed by elaborate machinery to be ground

to the finest powder sifted, and weighed into sacks Lampblack is used for making printer's ink, stove and shoe polish, paints, and in fact nearly everything in which a black pigment for colouring matter is required. Lampblack is one of the purest varieties of amorphous carbon The analysis of a sample of acetylene "soot" furnishes 1 4 per cent of hydrogen, and 98 6 per cent of carbon The hydrocarbons can be removed by heating the substance in a current of chlorine

§ 2 Charcoal

Wood charcoal —There are two main varieties of charcoal—wood and bone Wood charcoal is made by burning wood with a limited supply of air in a charcoal pit or kiln; or by heating wood in closed vessels so that air is excluded In illustration, place a few bits of wood at the bottom of a porcelain crucible Cover the wood with a layer of fine sand so as to cut off the supply of air Heat the crucible until combustible gases cease to be evolved. When cold, a small piece of charcoal remains in the bottom of the crucible Note the shrinkage in volume during the carbonization by comparing a piece of charcoal with a bit of wood like that heated in the crucible preserved as duplicate Charcoal resists the action of moisture, etc better than wood, and hence wooden piles, fence posts, and telegraph poles are often superficially charred before being put in the ground. Some claim this treatment gives the timber a longer useful life Charcoal is used as a fuel, in the manufacture of iron and steel, in the manufacture of gunpowder, in metallurgical operations, as deodorizer, filtering medium, etc (see below)

Pit charcoal —In outline the industrial preparation is as follows Small logs or billets of wood are loosely piled into vertical heaps and covered with sods and turf to prevent the free access of air A "shaft" is left in the middle of the pile to act as a central chimney or flue, and smaller holes are left round the bottom to admit the air. The pile so prepared is called a "charcoal pit" or a *Meiler* (German) The arrangement is not unlike the sulphur calcarone, Fig 147 The wood is lighted by brushwood at the centre, and just sufficient air to allow the wood to smoulder is passed through the pile The volatile matter escapes, and in about fifteen days the fire dies out Between 80 and 90 per cent of the weight of the wood, on the average, is lost by combustion, and the remaining 10 to 20 per cent is wood charcoal. The process can only be used where wood is cheap and abundant because the method is uncertain and wasteful. The process is still in use in a few places in Europe In Sweden rectangular piles are used, and the wood is placed horizontally and transversely

Kiln and retort charcoal —Some valuable gaseous and liquid products are lost in making pit charcoal. In modern processes, the wood is heated in ovens, kilns, or retorts, sealed from the outside air The operation may be conducted simply for charcoal without recovering the by-products, or the operation may be conducted somewhat similar to the process used for the manufacture of coal gas The products of the dry distillation of wood include: solid charcoal in the retort, liquids—wood tar (Stockholm tar from pine wood), water containing wood spirit, pyroligneous (acetic) acid, acetone and fatty oils, and gaseous wood gas—containing hydrogen, carbon dioxide, carbon monoxide, methane, acetylene, etc The wood

gas is used for illuminating purposes only when the temperature of distillation has been very high The products are approximately charcoal, 25·3, methyl alcohol, 0·8, acetic acid, 1·0, tar, 4·0, water, 45·9, wood gas, 23 per cent The charcoal in the retort retains the form of the wood from which it was prepared. Kiln charcoal is more compact than the pit charcoal—in the former case the charcoal weighs 20 lbs per bushel, and in the latter case, 16 lbs per bushel The yield of charcoal is about 81 per cent by volume, 28 per cent by weight

The dry distillation of wood can be well illustrated by placing some pieces of pine wood in a hard glass retort fitted with a receiver, etc, as shown in Fig 255 The tar and aqueous products condense in the receiver, and the wood gas itself can be lighted The watery liquid obtained by the dry distillation of wood is redistilled. The first portion of the distillate is the so called "wood spirit" The wood spirit is purified by distillation from recently ignited quicklime, and by the evaporating of a mixture of the wood spirit with fused calcium chloride to dryness The resulting compound ($CaCl_2 \cdot 4CH_3OH$) is decomposed by treatment with water, and the solution is distilled Finally, the distillate is rectified by repeated distillation over fresh quicklime The resulting methyl alcohol, CH_3OH, boils at 66·78°

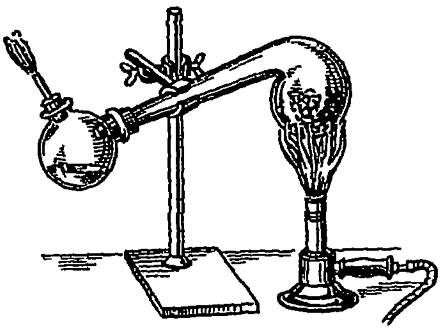


FIG 255 —Dry Distillation of Wood

Bone or animal charcoal —This is made by heating bones, blood, etc, in closed retorts. The bones may or may not have been subjected to a preliminary extraction with naphtha or benzene to remove the fat—degreased bones, or with superheated steam or water to remove gelatine (glue)—degelatinized bones. The products of the distillation include solid bone charcoal in the retort, liquids—a number of ammonium salts, bone oil, bone pitch, pyridine, etc, and gases of various kinds Bone charcoal contains about 10 per cent of carbon so that it is questionable if it ought to be included with the varieties of carbon at all However, the carbon is very finely divided and disseminated through a porous mass of about 80 per cent. of calcium and magnesium phosphates, and it seems to have specially valuable qualities. Bones furnish *boneblack*—sometimes called ivory black—the term *ivory black* is usually applied to the product obtained by digesting bone black with hydrochloric acid to remove the calcium phosphates. Blood furnishes *blood charcoal* For the uses of bone black and animal charcoal, see below, ivory black is used as a pigment, in the manufacture of blacking, etc.

§ 3 The Properties of Amorphous Carbon

The specific gravity of carbon is greatly influenced by the temperature to which it has been heated, amorphous carbon varying from a specific gravity 1·45 to 1·70 Although charcoal *per se* has a greater specific gravity than water, ordinary charcoal will float on water because it is

buoyed up by the air in its pores. If charcoal be weighted with a bit of lead and boiled in water for a few minutes, the air will be displaced by water and the wet charcoal will sink when placed in cold water. A stick of charcoal can also be "anchored" below the surface of water in a tall cylinder by means of a piece of string and a weight at the bottom of the cylinder The stoppered cylinder is then connected with an air pump, Fig 256 The bubbles of gas rise through the water As the air is removed, the charcoal gradually sinks to the bottom of the cylinder.

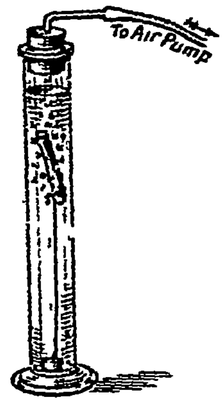


FIG 256 —Gases absorbed by Charcoal

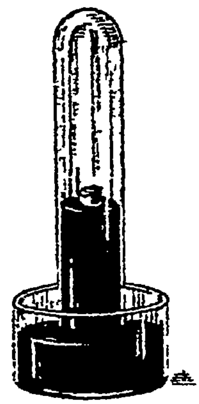


FIG 257 —Absorption of Ammonia by Charcoal

Absorption of gases —Charcoal has a remarkable power of absorbing gases, etc. A fragment of charcoal recently heated to expel air from its pores, is placed under a cylinder of ammonia gas, Fig 257. The ascent of the mercury in the cylinder is a striking demonstration of the absorption of gas by the charcoal The phenomenon is sometimes styled adsorption, meaning that the gas adheres in some unknown way to the surface of the charcoal One volume of cocoanut charcoal absorbs (Hunter)

	Volumes at 0°, 760 mm.
Ammonia	171
Ethylene	75
Carbon dioxide	68
Carbon monoxide	21
Oxygen	18
Nitrogen	15

At low temperatures the absorptive power of charcoal for some gases is very much greater Thus, a gram of charcoal which absorbs 18 c c of oxygen at 0°, will absorb nearly 13 times as much, namely 230 c.c at −185°, the corresponding numbers for hydrogen are 4 c c at 0°, and 135 c c at −185° This property affords a means of producing high vacua, and also of separating gases which are not readily absorbed (helium, neon) from those which are readily absorbed (air, etc)

It appears as if the gases which are absorbed in greatest quantity by the charcoal are approximately those most easily condensed to the liquid state, and, rightly or wrongly, it is sometimes stated that the gases are actually liquefied on the surface of the charcoal In any case, the "condensed" gas is usually more chemically active than the gas in the ordinary condition Thus if charcoal be allowed to absorb chlorine, and then be brought in contact with dry hydrogen, the hydrogen and chlorine combine to form hydrogen chloride under conditions where they would not otherwise react. If charcoal which has been saturated with hydrogen sulphide be brought into oxygen gas, the rapid combination develops so much heat

that the charcoal is inflamed Sewers and foul places are sometimes temporarily purified—"sweetened"—by charcoal, charcoal biscuits have been recommended medicinally for absorbing gases in the alimentary canal in cases of flatulence

Absorption of liquids and solids—Charcoal also absorbs solids and liquids in a similar way A solution of litmus (indigo, tea, vinegar, etc) passes through filter paper without any noticeable change in the colour of the solution, but if the solution be filtered through charcoal, or if some recently ignited animal charcoal—say 10–20 grams—be shaken up with 50 c c of litmus solution and filtered, the filtrate is colourless A solution of acid quinine sulphate has a bitter taste, but after filtering through animal charcoal the solution no longer tastes bitter, 10 c c of an aqueous solution of lead nitrate (0 5 gram of the salt per litre) after boiling with 10 grams of animal charcoal and filtering, will give no precipitate with hydrogen sulphide—the original solution will Advantage is taken of this property of animal charcoal or bone black to remove the colouring matter from many products manufactured industrially *E g* coloured solutions of brown sugar are "bleached" on boiling with animal charcoal The charcoal removes the brown resinous colouring matter, and the evaporated syrup furnishes white sugar, fusel oil can be removed from whisky by filtration through animal charcoal before the whisky is rectified Charcoal filters are used for removing organic matter, etc, from drinking water But since a given mass of charcoal cannot absorb an unlimited supply of organic matter, frequent cleaning is required to maintain the efficiency of the filtering medium, otherwise the charcoal charged with organic matter may serve as a culture bed for bacteria, and do harm rather than good Consequently, the charcoal is cleansed from time to time by calcination at a red heat, otherwise, it becomes clogged, contaminated, and ineffective

Combustion—Ordinary charcoal burns readily in air and in oxygen without smoke The temperature at which combustion starts is largely determined by its physical condition, if the charcoal be very finely divided, it may ignite spontaneously in air The higher the temperature to which charcoal has been heated, the higher the temperature at which it ignites in oxygen Sugar charcoal which has been heated in the electric furnace, and graphites generally, must be heated to 660° before combustion can start

Carbon a reducing agent—The "affinity" of carbon for oxygen is so great that it can take the oxygen from many metallic oxides Hence in metallurgical industries, carbon is often used as a reducing agent for ores of iron, copper, zinc, lead, etc When a mixture of carbon with one of these oxides, say, lead, is heated in a crucible, either carbon monoxide or carbon dioxide is evolved, and the metal remains behind

$$PbO + C \rightarrow Pb + CO\text{, or, } 2PbO + C = 2Pb + CO_2$$

Carbides—Carbon also unites directly with many elements at high temperatures—*e g* with sulphur to form carbon disulphide (p 688), with nitrogen to form cyanogen (p 767), with hydrogen to form acetylene (p 696), with silicon to form carborundum, and with metals to form carbides *Carbides are compounds of carbon with other elements—chiefly metals* The most important of these, commercially, are silicon carbide

and calcium carbide Many of the carbides react directly with water forming hydrocarbons—methane (p 692), acetylene (p 697), etc.

Calcium carbide—CaC_2—is made by heating a powdered mixture of, say, 56 parts by weight of quicklime and 36 parts of coke in an electric arc furnace—estimated temperature 3000°—arranged so that the carbide, as it is made, moves away from the electric arc to enable a new charge to take its place The reaction is represented by the equation $3C + CaO \rightarrow CaC_2 + CO$ The process can be imitated on a small scale by clamping a graphite crucible to an iron rod, and connecting it with the — pole of a current of 60 to 100 volts The + pole is an electric light carbon rod which is clamped to a retort stand—Fig 258 The retort stands rest on some insulating material. The carbon rod is allowed to touch the bottom of the crucible and withdrawn, by the insulated handle *a*, so as to form an arc The mixture of coke and quicklime is then gradually added to the crucible

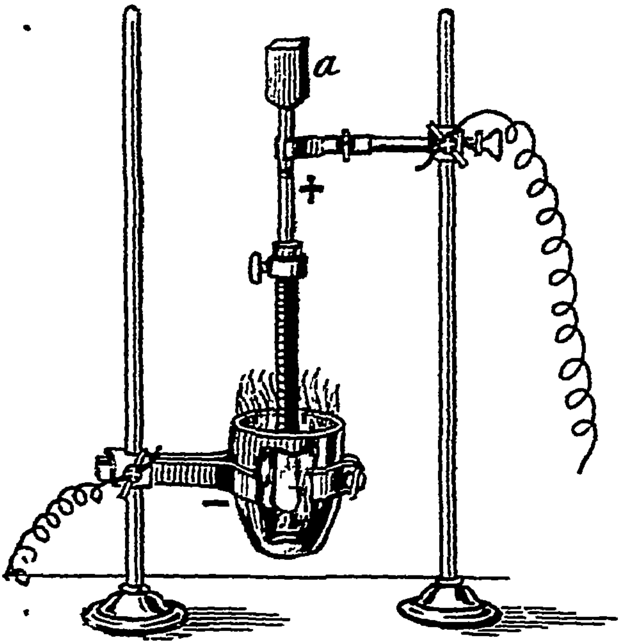


FIG 258 —Preparation of Calcium Carbide

Calcium carbide is a hard, brittle, crystalline solid, specific gravity 2 2 When pure, it is white, but commercial calcium carbide is dark grey or bronze coloured owing to the presence of impurities Calcium carbide reacts with water forming acetylene (p 697), and it is sold packed in tin cans to protect it from deterioration by exposure to the moisture of the atmosphere Calcium carbide is also used in the manufacture of calcium cyanamide used as a fertilizer, and in the manufacture of cyanides.

§ 4 Coal and its Relations.

Vegetable origin of coal —Geologists have potent reasons for believing that coal is of vegetable origin The softer varieties of coal are often changed so little that their vegetable origin is easily seen. Fossil plants can be recognized, and photographs of thin slices under the microscope show clearly the vegetable character of the coal. In some of the harder varieties, the vegetable origin can only be demonstrated by analogy and comparison with varieties less modified. There is a closely graded series ranging between peat at one end, and the anthracitic coals, or may be graphite, at the other It is convenient, however, to pick out certain

members of the series as types We thus obtain peat, lignite, bituminous, and anthracitic coals There are no hard and fast lines between these different types, the one merges into the other by insensible gradations, The chemistry of the process appears to be somewhat as follows

Metamorphosis of vegetable tissue into coal —When vegetable tissue is exposed to the air, it oxidizes and decays comparatively quickly, the gaseous products of the oxidation diffuse into the atmosphere, and the mineral constituents remain behind. If the oxidation takes place in a limited supply of air, *e g* while submerged in a swamp or bog, the process of decomposition is rather different Some of the carbon is oxidized to carbon dioxide, and some of the hydrogen is oxidized to water, and probably some is transformed into methane—marsh gas—etc As a result an increasing proportion of carbon remains behind The total weight of the organic matter decreases, and, although the total amount of mineral matter—ash—remains constant, the *percentage* amount increases These changes are represented diagrammatically in Fig 259 (after J S Newberry, 1883) Assuming that vegetable tissue contains approximately 50 per cent of carbon, and 50 per cent. volatile hydrocarbons, moisture, etc, the loss of these components, in passing to peat, is represented by the downward slopes of the lines *AB*, and *CD* These lines illustrate the changes in the proportions of volatile matters and fixed carbon in the vegetable tissue as it changes to peat → lignite → bituminous coal → anthracite → graphite Table LIV represents averages from between 6 and 20 published analyses of the different varieties of coals, etc, named, and they therefore represent no particular variety

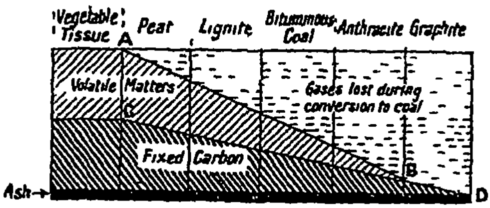


FIG 259 —Metamorphosis of Vegetable Tissue (After Newberry)

TABLE LIV —AVERAGE COMPOSITION OF DIFFERENT TYPES OF COAL.

	Ash	Fixed carbon	Volatile matter	Moisture
Wood	1 5	25 0	53 5	20 0
Peat	1 2	29 2	51 5	18 1
Lignite	8 0	43 1	42 7	6 2
Bituminous coal	6 3	63 5	29 2	4 0
Anthracite	5 4	86 5	6 1	2 0

Origin of the different varieties of coal —While it is probable that the early stages of the metamorphosis are brought about by bacteria and oxidation in a limited supply of air, it is also probable that the *pressure* of the superincumbent deposits of sand, mud, etc, extending over *long* periods of time, are needed for the later transformations The gases—carbon

dioxide, methane, water, etc —formed during the earlier stages of the process of conversion of vegetable tissue to coal, can escape, later, when the air is shut off, methane, etc, may be imprisoned in the coal to be released as "firedamp," p 691, when the pressure is relieved during the mining of the coal In some cases, the coal appears to have been *heated under pressure*. The nature of the final product, as now mined, must depend on the character of the original deposits and on the particular conditions which prevailed at the different stages of the process of transformation The vegetable matter may have been deposited in fresh or salt water, in lakes, lagoons, seas, in marine swamps, etc The original vegetable tissue may have been algæ deposits in sargossa seas, peat bogs, vegetable accumulations on the soil in luxuriant forests, delta and drift deposits, etc The pressure may have been comparatively small, extended over a long period of time, and applied comparatively early in the process of transformation, the pressure may have been very great and applied late in the process of conversion, etc An "old" coal geologically, might be "young" chemically, and conversely Geologists can sometimes form a good idea what has happened, in other cases, they confess complete ignorance.

The different types of coal —Assuming that peat represents the first stage in the metamorphosis of vegetable tissue into coal, it is possible to recognize several different types of peat ranging from bog-moss to heavy black peat which is closely related to **lignite or brown coal**—the second stage in the process of conversion Analysis shows that lignite contains a large amount of moisture, and although it ignites readily, and burns with a long smoky flame, its calorific power is comparatively low Lignite generally disintegrates rapidly on exposure to the air **Bituminous coal** —the third stage in the transformation—is denser than lignite, black, and comparatively brittle It seldom disintegrates on exposure to the air like lignite Thin sections under the microscope show traces of woody fibre, lycopodium spores, etc It burns with a yellow flame, and has a greater heating power than lignite Some bituminous coals when heated, soften and seem to fuse, for the coal cakes into a continuous mass—**caking or coking coal** Caking coals furnish a hard compact coke Other bituminous coals do not cohere in this way when heated—**non-caking coals** These furnish a pulverulent coke There are all gradations between the two sub types **Anthracite coal** has a low proportion of volatile hydrocarbons, and a greater amount of fixed carbon than the other varieties It is hard, dense, black, and brittle, it presents no trace of vegetable structure, it ignites with difficulty and burns with a short flame with a high calorific power

Parrot or cannel coals differ from ordinary bituminous coals, and appear to have been formed differently Cannel coals from different localities pass by insensible gradations into bituminous shales. Cannel coals burn with a luminous smoky flame, hence the term "cannel coal" (candle), they also decrepitate with a crackling noise when heated, hence the term "parrot coal" These coals are used almost exclusively for gas making Cannel coals yield a relatively large quantity of highly luminous gas, leaving a residue which contains a relatively small amount of coke They contain from 50 to 70 per cent volatile matters, 30 to 50 per cent of fixed carbon, $1\frac{1}{2}$ to 5 per cent of ash, up to $1\frac{3}{4}$ per cent of sulphur and 3 per cent of moisture

§ 5 Coke

Coke is the residue obtained when coal is heated in a closed vessel out of contact with air Coke generally contains about 90 per cent of carbon Coke is used in the manufacture of iron and steel, and in a great many metallurgical operations where its comparative freedom from sulphur and certain other impurities render it more suitable than coal. Coal may be converted into coke by heating it in closed vessels—gas, tar, and ammonia are obtained as by-products, or if coal gas is being manufactured, coke, tar, and ammonia are the by-products The properties of coke depend upon the nature of the coal from which it is obtained, and upon the way the coal is "coked" The two main varieties are *soft coke*—porous, black, brittle, ignites with difficulty, and is used for smith's forges, etc, *hard coke*—dark grey in colour, bright lustre, compact, metallic ring when struck, bears great pressure without crushing, used for furnace work and metallurgical operations generally Coke may or may not be prepared under conditions where the by products are recovered The two following processes typically represent the two systems of "coking"

The beehive oven—so called on account of its shape—furnishes an excellent coke, but is rather wasteful The ovens are built in batteries back to back with from 20 to 200 ovens Each oven cokes about 7 tons of coal, and furnishes 4 or 5 tons of coke The air for burning the coal enters through an opening in the door, and the gases escape through the top flue fitted with a damper The air supply is diminished from day to day. When no flame is visible, and all the interior is red hot, the openings are luted with clay, and in 24 hours (70–84 hours in all) the door is opened, and water from a hose is sprayed in the oven which is then ready for discharging

Coking in retorts—Simon-Carves' oven —The retorts are horizontal chambers built side by side in batteries of 22 to 50 The retorts are worked in pairs—one is discharging when the other is half "coked." The retorts are closed except for the exit left for the escape of the volatile products of distillation The products of distillation are passed through condensers, and the gases are returned to be burnt in the horizontal flues below the retorts There is a system by which the waste heat from the products of combustion warms up the air—secondary air—which is employed for burning the gas below the retorts In about forty eight hours, the coke is expelled from the retort by means of a ram, and at once quenched with water The retort is recharged through hoppers in the roof The yield is almost theoretical The by-products are recovered. The coke is black, hard, compact and without metallic lustre

§ 6 Graphite

Graphite is widely distributed in different parts of the world. Large deposits occur in Ceylon and other parts of India, Eastern Siberia, United States, Canada, Bavaria, Bohemia, Moravia, Pinerola (Italy), etc The mines at Borrowdale (Cumberland) are practically exhausted Graphite also occurs in the form of fine crystals in many meteorites The ultimate composition is represented by the following analyses

	Volatile matter	Carbon	Ash
Cingalese (Commercial)	5 20	68 30	26 50
Bohemian (Schwarzbach)	1 05	89 05	9 90

But more pure and less pure varieties are on the market It was once supposed that graphite contains lead—hence graphite is sometimes called *blacklead*, and *plumbago*

Graphite varies in specific gravity from 2 to 3 Hard graphite and soft diamonds have nearly the same specific gravity Graphite occurs in two forms called crystalline and "amorphous" The crystalline variety has a lamellar, scaly, or flaky structure, and is largely used in the industries The "amorphous" variety is not of much industrial importance

Action of reagents —Pure graphite is not attacked by heating it in a current of chlorine, nor by fusion with potassium or sodium hydroxide, some varieties are attacked by fused nitre Chromic acid or a mixture of sulphuric acid and potassium dichromate oxidize it to carbon dioxide Neither dilute nitric nor dilute sulphuric acid attacks graphite although some varieties swell up into worm-like structures—sometimes 12 cm long —when the finely granulated (not powdered) graphite is moistened with nitric acid (specific gravity 1 52–1 54) in a platinum dish, and then heated W Luzi (1891) calls those varieties which are indifferent to the nitric acid treatment—graphitites, and those which swell up—graphites It is generally believed that the phenomenon is a physical effect due to the absorption of acid in the capillary pores and subsequent expansion through the development of gas under the influence of heat

Graphitic acid —The action of nitric acid on graphite is characteristic and distinguishes graphite from amorphous carbon, even though the different varieties of graphite differ considerably among themselves Finely powdered graphite is intimately mixed with 3 parts of potassium chlorate and sufficient concentrated nitric acid to give a liquid mass After heating three or four days on a water bath, the solid residue is washed with water, and dried The treatment with nitric acid, etc, is repeated four or five times until no further change occurs Finally, a yellow substance is obtained which retains the form of the original graphite [1] It is called graphitic acid (B Brodie, 1859) The composition of graphitic acid is not quite clear [2] The subject has not been investigated very much For convenience, the above treatment is sometimes called Brodie's reaction Diamonds are not attacked by the treatment and ordinary charcoal gives a brown mass soluble in water Brodie's reaction is a valuable means of identifying graphite, and it is considered the safest test for graphite known at the present time. Some graphites (*e g* Bohemian) give yellow amorphous powders, others (*e g* Cingalese) give yellow microscopic lamellar crystals If graphitic acid be heated, it swells up, forming a finely divided black powder resembling graphite, and called Brodie's graphite or pyrographitic acid The graphite which results from the treatment of amorphous graphite is almost identical with ordinary lampblack so far as colouring and covering power are concerned, while the graphite from crystalline graphite lacks these two qualities—colouring and covering power

The action of heat —Graphite when heated in air or oxygen, burns to carbon dioxide, but it undergoes no change when heated in the absence of air or oxygen It is rather difficult to ignite. The ignition temperature approaches 600°–700° If some varieties of powdered graphite be heated

[1] One treatment suffices for some graphites, others are more resistant.
[2] W Luzi gives $C_{24}H_9O_{13}$, M Berthelot, $C_{28}H_{10}O_{13}$

in a test-tube to about 170°, the grains swell up enormously in bulk and fill the test tube with a light amorphous powder—hence the term *sprouting graphite*

Artificial graphite—Iron dissolves considerable quantities of carbon particularly if much silica be present The higher the temperature, the greater the amount dissolved. On cooling, part of the carbon is rejected chiefly in the form of graphite (see "Iron") Black scales of graphite can be seen on a freshly fractured surface of cast iron, and masses of it accumulate near the base of blast furnaces where it is called "kish" Graphite is also formed when coke or charcoal is heated to a very high temperature in the electric furnace out of contact with air Acheson's graphite is made at Niagara Falls by first grinding coke with coal tar or molasses, moulding the paste into any required shape, and baking the mixture in suitable ovens. The carbons so prepared are used for batteries, electric arc lights, etc They are graphitized, if required, by heating in the electric furnace

Uses—Graphite when rubbed on paper leaves a black mark—hence the term graphite—from γράφειν (graphein), to write It is therefore used for making *lead pencils* For this purpose the natural graphite is purified by grinding and washing so as to remove the grit The purified graphite is mixed with a little washed clay and forced by hydraulic pressure through dies of the necessary shape It is then stoved and cased in wood (red cedar for preference) Scaly graphite has been largely used, on account of its refractory qualities and high heat conductivity for the manufacture of *plumbago crucibles* The graphite is mixed with different proportions of clay and sand—*e.g* 75 parts of plastic clay, 25 sand, and 100 of graphite. The crucibles are moulded by machinery or by hand, dried, and baked at a red heat Other refractory goods are also made from graphite Graphite is also used as a lubricant for machinery, a coating for iron to prevent rusting, coating for goods—say plaster of Paris—to be later electrotyped, preventative for boiler scale, stove polish, polishing powder for gunpowder, etc Graphite is also used largely in making electric furnaces either alone or mixed with carborundum—thus *kryptol* is a mixture of graphite, carborundum, and clay The resistance offered by this material to the passage of the electric current raises the temperature of the mass If the mixture be suitably enclosed very little graphite is lost by combustion Graphite conducts electricity very well, and electrodes of graphite are used in the electrochemical industries—*e g* as anodes in the manufacture of chlorine by electrolysis of sodium chloride Graphite is also used for battery plates, electric light carbons, etc

§ 7 The Diamond

For long ages diamonds have been prized as ornaments on account of their beauty, rarity, and permanence Diamonds occur in their natural state as more or less rounded rough looking pebbles not unlike pieces of gum arabic in appearance The natural diamond must be cut and polished to bring out its lustre and sparkle The shape of the crystal as it leaves the diamond cutter has no relation to the natural crystalline shape The object of the lapidarist is to get the maximum reflection of light from the interior of the stone The "brilliant," for instance, is a standard shape

with a rather large flat face which is really the base of a pyramid with many sides (facets) The high reflecting and refracting power of the diamond are the particular qualities which make it supreme above other gems In virtue of these qualities, the light falling on, say, the front face of a brilliant passes into the diamond, and is reflected from the interior surface of the facets. The reflected light is refracted into a wonderful play of "lightning flashes, and sparkling scintillations" as it passes into the air The Cullinan is the largest known diamond. It was found near Pretoria (South Africa), January, 1905, and weighed over 1¼ lbs ; but stones over an ounce [1] in weight are comparatively rare

Occurrence —Diamonds are sparsely distributed in different parts of the world. The chief localities are South Africa, Brazil, Ural, India, Borneo and Australia They have been found in meteorites—*e.g* the Canyon Diablo meteorite (Arizona, U S A), contained both black and transparent diamonds Diamonds occur in river beds and in beds or pipes containing a heterogeneous mixture of fragments of various rocks cemented together with a bluish indurated clay known as "blue earth" The diamonds are found embedded in the blue clay The clay crumbles on weathering, and the diamonds are readily detected in the disintegrated mass

Varieties —Diamonds are usually tinged slightly yellow The clearest and most nearly colourless diamonds without flaw are most prized as "diamonds of the first water" Diamonds are also occasionally coloured blue, pink, red, and green owing to the presence of traces of foreign metals Some diamonds are dark grey and even black. They exhibit a more or less imperfect crystalline structure, and are known as *black diamonds*—boart or bort, and carbonado *Boart* is an imperfectly crystallized black diamond which has various colours, but no clear portions, and is therefore useless as a gem, boart is used in the drilling of rocks, and in cutting and polishing other stones *Carbonado* is the Brazilian term for a still less perfectly crystallized black diamond It is as hard as boart, and has similar uses Boart and carbonado are usually regarded as intermediate forms between diamonds and graphite

Properties —The diamond is rather brittle It is the hardest substance known Crystalline boron comes next, it is nearly as hard as the diamond The hardness, refracting power, and other properties vary with different diamonds, and, indeed in different parts of one diamond. The specific gravity varies from 3 514 to 3 518, carbonado, 3 50, boart, 3 47 to 3 49 Amorphous graphite has a specific gravity of 2 5, hard gas carbon, 2 356, and amorphous carbon, 1 45 to 1 70 The diamond is transparent to Röntgen's rays, whereas glass, used in imitation of the diamond, is nearly opaque to these rays This furnishes a ready means of distinguishing imitation diamonds from the true gems

The diamond is insoluble in all liquids Fused potassium difluoride mixed with 5 per cent of nitre attacks the diamond slightly, a mixture of potassium dichromate and sulphuric acid oxidizes the diamond to carbon dioxide at about 200° Unlike graphite and amorphous carbon, diamonds are scarcely attacked by a mixture of potassium chlorate and nitric acid

The action of heat —If a clear crystal of the diamond be placed

[1] Diamonds are sold by the "carat" One carat corresponds with 0 207 gram or 3⅕ grains troy The term "carat" is derived from the carob bean, formerly used as a small weight by the diamond merchants of India

between two carbon poles of an electric arc—in the absence of air—when the temperature approaches 2000°, the diamond swells up and changes to black graphite The diamond, boart, and carbonado commence to burn when heated in air between 710° and 900° The ignition temperature depends upon the hardness, etc, of the diamond. A soft Brazilian diamond burnt at 710°, and an exceptionally hard boart at 900° It is rather difficult to burn the diamond unless the temperature be maintained by, say, placing the diamond on a piece of platinum foil heated red hot by an electric current An apparatus suitable for the purpose is illustrated in Fig 260 A splinter of diamond is placed on a piece of stiff platinum foil arranged so that it can be heated red hot by the passage of an electric current Some varieties of graphite require a special method of ignition before they can be burnt in oxygen gas The product of the combustion is carbon dioxide (p 653) A light ash consisting of iron, lime, magnesia, silica, and titanium remains. Clean crystalline diamonds have about 0 05 per cent of ash, whereas with boart the ash may run as high as 4 per cent Arguing from the high refractory power of camphor, olive oil, amber, etc, "which are fat, sulphureous, unctuous bodies," Isaac Newton (1675) inferred that "a diamond is probably an unctuous substance coagulated" Thus predicting what was later on proved experimentally

FIG 260—The Combustion of Diamonds in Oxygen

The synthesis of diamonds—Molten solids, on cooling, generally crystallize Carbon, however, volatilizes at ordinary atmospheric pressures at about 3600° without passing through an intermediate liquid state Arsenic also volatilizes at ordinary pressure without liquefying, but arsenic easily liquefies if it be heated under pressure It is therefore inferred that if sufficient pressure could be obtained, carbon also would melt to a liquid which would crystallize on cooling The diamond at ordinary temperatures is supposed to be the unstable, and graphite the stable form If the one form does pass into the other at ordinary temperatures, the speed of transformation must be extremely slow A Smits' hypothetical views (1905) are summarized in Fig 260A. It is estimated that if the pressure were great enough, graphite would melt at about 3000°, and that the liquid would have a vapour pressure represented by *BC*, Fig 260A, and the solid a vapour pressure *AB* The vapour pressure of the diamond would be represented by *AD* where *D* is the melting point of the diamond under great pressure *BE* shows how the melting point of carbon changes with pressure. If molten graphite be under cooled the solution would become more and more viscous, and appear as amorphous carbon.

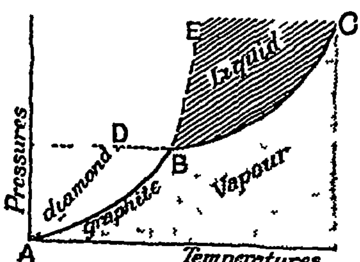


FIG 260A

Iron dissolves carbon and gives it up again on cooling Other metals, especially silver, behave in a similar manner, but iron appears to be the best solvent The solubility increases with the temperature Moissan

packed a piece of iron, as pure as practicable, in a carbon crucible with sugar charcoal The crucible was heated between the poles of an electric arc furnace (700 amps, 40 volts)—Fig 261 Under these conditions the iron melted and dissolved much carbon When the temperature had reached 4000°, and the iron was volatilizing in clouds, Moissan plunged the crucible in cold water The sudden cooling solidified the outer layer of iron The expansion which the inner liquid core underwent on solidifying must have produced an enormous pressure Hence, the carbon separated from the iron under a very great pressure After dissolving away the iron, etc, some of the carbon which remained was in the form of boart—black diamonds—some as graphite, and some in the form of transparent diamonds—microscopic it is true Moissan separated as many as 10 to 15 minute transparent diamonds from a single ingot treated in this way The largest was about $\frac{3}{4}$ mm long Crookes also appears to have detected diamonds in the carbonaceous residue obtained when cordite is exploded in closed steel cylinders where the pressure is estimated to be as high as 8000 atmospheres and the temperature over 4000°

E de Boismena (1907) claims to have synthesized diamonds approaching 2 mm in diameter by the electrolysis of molten calcium carbide The diamonds were found about the anode A kilogram of the carbide is said to have furnished 1 75 carats of true diamonds The claim is unconfirmed

§ 8 Electric Furnaces

The use of electrical energy for metallurgical furnaces is becoming of greater importance every day The heat required for the reduction of the metals from their ores, and for the subsequent treatment of the metals is no longer exclusively produced by the combustion of carbonaceous fuels—charcoal, coal, coke, gas, petroleum, etc Carbonaceous fuel is apparently used in some electric smelting furnaces, but rather as a reducing agent and carbonizer than as a source of heat The most important characteristic of electric energy is the concentration of almost any degree of heat in a given space so that operations can be readily performed which are impossible at the lower temperatures available with carbonaceous fuels The applicability of the electric furnace for ordinary metallurgical operations—reduction of iron ores, etc —is feasible where cheap water power is available and fuel is costly, although usually, electrical power is too costly for ordinary smelting operations

It seems here advisable to emphasize the difference in some types of electric furnace indicated in this work Furnaces in which the electric current is used as a source of heat are not to be confused with those in which the electric current is used for electrolysis The main types of electric furnace are

1 Arc furnace —In this, the heat is produced by one or more electric arcs The arc may be established between one or more pairs of carbon or graphite poles as in Moissan's furnace—Fig 261, or between the fused metal bath or fused slag and a carbon pole as in some furnaces used for reducing iron ores to pig iron, and in refining pig iron and steel

2 Resistance furnace —Here the heat is produced by the passage of an electric current through a solid or liquid resister

(a) A special resistance, e g nickel, ni chrome, platinum wire, fragments of carbon, etc, is embedded between the inner and outer walls of the furnace The inner wall may take the form of a muffle, tube, etc These furnaces are fairly common in chemical laboratories

(b) The charge in the furnace constitutes the resisting medium The resistance of the medium raises the temperature of the charge, e g the phosphorus furnace (Fig 213), the calcium carbide furnace (Fig 258), the calcium disulphide furnace (Fig 242), and the carborundum furnace (Fig 302)

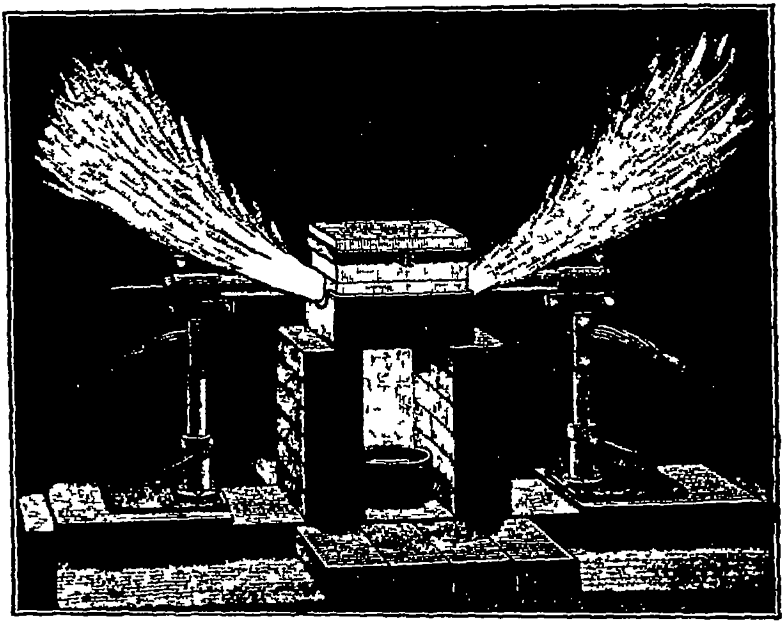


FIG 261 —Moissan's Electric Arc Furnace

3 Electrolytic furnace.—A continuous current splits the fused electrolyte into its component parts The heating effect of the current may or may not suffice to keep the contents of the furnace in a fluid condition The aluminium furnace (Fig 224) illustrates the former, and Castner's sodium furnace (Fig 134) the latter

4 Transformer or induction furnace —The molten metal forms part of the secondary of a large transformer, and the current is not led in by terminals or electrodes, but by wireless transmission is generated directly in the metal bath The furnace hearth is thus connected with the dynamos in no visible way These furnaces are used in steel refining, and are not illustrated in this text-book.

Question

1 What do you understand by the terms element and compound ? What experiments would you make on (a) ferric oxide and (b) carbon in order to determine in the case of each of these substances whether it is an element or a compound ?—*Univ North Wales*

CHAPTER XXXVIII

COMBUSTION AND FLAME

§ 1 Mayow's Work on Combustion.

Slowly, gradually and laboriously one thought is transformed into a different thought, as in all likelihood one animal species is gradually transformed into a new species Many ideas arise simultaneously They fight the battle for existence not otherwise than did the Ichthyosaurus the Brahmin, and the horse Thoughts need their own time to ripen, grow, and develop —E MACH

NEAR the beginning of the sixteenth century, Leonardo da Vinci clearly recognized that air is necessary for the sustenance of the flame of a burning candle, for he said "there is smoke in the centre of the flame of a wax candle because the air which enters into the composition of the flame cannot penetrate to the middle It stops at the surface of the flame and condenses there" R Boyle (1661) also noticed that owing to the "want of air" the flame of a lighted candle expired more quickly under the exhausted receiver of an air pump than when the receiver was not exhausted. This and other experiments on similar lines showed that, air is necessary for combustion Robert Hooke (1665) suggested that air was mixed with a substance "which is like, if not identical with, that which is fixed in saltpetre"[1] John Mayow (1674) subjected the guess or hypothesis of Hooke to the test of experiment

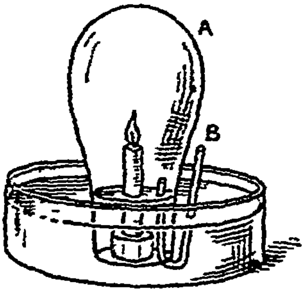


FIG 262 —Mayow's Experiment on Combustion

Mayow arranged a candle in water so that the wick was between 9 or 10 cm. above the surface of the water. A glass cylinder, *A*, Fig 262, was lowered over the burning candle so that the level of the water inside and outside the cylinder was the same[2] The flame of the candle soon expired and water rose in the jar. Some gas still remained in the jar, but it could not be air because one of the characteristic properties of air is to support the burning of the candle, and the flame of a candle is immediately extinguished in the residual gas. Hence Mayow inferred that air contains two kinds of particles one of which—the "nitro-aerial particles"—is "withdrawn and destroyed"[3] by the burning candle. Mayow does not seem to have quite

[1] Scheele later produced oxygen from saltpetre—that is, potassium nitrate

[2] Mayow describes a small syphon *B*, Fig 262, which he used for this purpose Immediately the jar was in position, the syphon was removed

[3] " *ab aere exhauriri et absumi* "

grasped the idea that "the nitro aërial particles" which support combustion actually combine with the burning body, although he correctly inferred that the air was a mixture of nitro aërial and aërial particles[1]

In fine, Mayow's observations show that air is a mixture of two gases one of which is withdrawn during combustion, and the remaining gas does not support combustion Mayow got very near to the present-day theory of combustion, but unfortunately, his ingenious experiments had very little, if any, influence on the subsequent development of chemistry, because, for another century, more trust was placed in phantasms of the imagination than in facts obtained by precise observations

§ 2 The Phlogiston Theory

> During the greater part of the eighteenth century, the doctrine of phlogiston was not only the lamp and guide of chemists but it remained the time honoured and highest generalization of physical chemistry for over half a century —S P LANGLEY

> Phlogiston died as an old king—once infinitely dominant somewhat tyrannical, not always just, now deposed, decrepit, utterly senile, forsaken by all —W ODLING

Up to the middle of the eighteenth century, combustion was explained by the aid of Plato's assumption that all combustible substances contained a common element—an inflammable principle—which enabled them to burn This obviously means very little more than that substances burn because they are combustible Geber (c 770) thought that the inflammable principle must be sulphur—*ubi ignis et calor, ibi sulphur* ("where there is fire and heat, there is sulphur") J J Becher (1669) pointed out that many combustible substances were known which did not contain sulphur, and he was led to postulate the existence of another principle which he termed *terra pinguis*—fatty or inflammable earth. Becher's fatty earth became Stahl's phlogiston—from the Greek φλογίστεω (phlogisteo), I set on fire G E Stahl (1723) taught that in the act of combustion phlogiston, an intrinsic constituent of combustible bodies, was set at liberty Oxidation was said to be due to the escape of phlogiston, reduction to the absorption of phlogiston. When a metallic oxide was heated with a substance rich in phlogiston, *e.g* charcoal—or reducing agents generally—the charcoal supplied the calx or metallic oxide with phlogiston, and reproduced a compound of phlogiston with the metallic oxide which was the metal itself Metals were thus supposed to be compounds of phlogiston and their calces (oxides) If phlogiston escaped, the metallic oxide remained The idea can be symbolized

$$\text{Metal} \rightleftharpoons \text{Phlogiston} + \text{metal calx (oxide)}$$

When it was shown that the metallic oxides were heavier than the corresponding metals (*e g* Rey's experiment) it was assumed that phlogiston was lighter than air so that the metal was buoyed up, so to speak, by the associated phlogiston (p 7)

Lavoisier's conclusive proof (1774) that the increase in weight which occurs during oxidation is equal to the weight of oxygen absorbed from the

[1] Some modern commentators consider the former to be oxygen, the latter nitrogen.

air, and his crucial demonstration that combustion is a process of absorption and increase in weight which cannot be explained by a supposed loss of substance soon banished the phlogiston hypothesis from the domain of science. It is not surprising that writers on chemistry in the Middle Ages failed to interpret the experiment of the burning of a candle in air when we recall the knowledge required to explain the chemical side of the phenomenon, altogether apart from the skill required in the manipulation of gases·

(1) Air is composed of two gases both sparingly soluble in water,
(2) During combustion, one of the gases unites and the other does not unite with the burning body,
(3) Air contains four volumes of the inert gas, and one volume of the gas which unites with the burning body,
(4) A gas soluble in water is produced during the combustion; and
(5) The increase in weight of the combustible body during combustion is equal to the decrease in the weight of the air

The phlogiston hypothesis is sometimes held up to ridicule We must bear in mind that the hypothesis was adopted by nearly all the leading chemists in the earlier part of the eighteenth century when it appeared to be as firmly fixed among the root principles of chemistry as the kinetic theory does to-day The phlogiston theory represented the most perfect generalization known to the best intellects of its day It is inconceivable that men like Bergmann Black, Cavendish, Priestley, and Scheele would counsel what they considered to be an inconsistent doctrine Phlogiston was regarded. not as a temporary hypothesis, but as a permanent acquisition, an enduring conquest of truth To-day, the word is but an empty symbol.[1]

Theories perish, facts remain —Much of what we think best in the theories of to-day, may to morrow be rejected, with phlogiston, worthless This need cause the student no embarrassment. A fallacious theory may be a valuable guide to experiment Experiment and labour applied to the explication of the most extravagent hypothesis need not be altogether lost. But it is necessary to follow René Descartes' advice Give unqualified assent to no proposition which is not presented to the mind so clearly that there is no room for doubt. As Aristotle would have said, we do not need to cultivate the art of doubting, but rather the art of doubting well

§ 3 Is Combustion Oxidation ?

Lavoisier's work in 1774, on the composition of air, and on the increase in weight which occurs when a metal is calcined in air, has already been described in outline. During the next two years, Lavoisier proved that carbon dioxide is the product of the oxidation of carbon—diamond and wood charcoal—and that carbon dioxide and water are the products of the combustion of organic compounds containing only carbon, hydrogen, and possibly oxygen. In 1777 Lavoisier published his oxidation theory

[1] Crum Brown (1866) has pointed out that "phlogiston" occupied a similar position in the chemistry of the eighteenth century that "potential energy" does to-day Here, then, the old revives in the new The chemistry of to-day is not materialistic, for it is occupied with both energy and matter

of combustion (1) Oxygen is necessary for combustion, (2) Oxygen is consumed during combustion, and the increase in weight of the substance burnt is equal to the decrease in weight of the atmospheric air The origin of the water formed during combustion was completely explained by Cavendish's synthesis of water in 1783 Consequently, **combustion is a process of oxidation which is attended by the development of light and heat** When carbon burns in air, carbon dioxide is formed, when hydrogen is burnt in air, water is formed, when phosphorus burns in air, phosphorus pentoxide is formed, sulphur furnishes sulphur dioxide, etc

It must be added that many other chemical reactions which furnish light, heat, and flame, are now also included under the term "combustion" even though oxygen be absent Hence **combustion is not always oxidation, for the term is applied generally to any chemical process which is attended by the development of heat and light** For instance, the "combustion" of brass in chlorine, of hydrogen in chlorine, etc The development of flame, light, and heat during combustion is quite an accidental feature of the process of oxidation The speed of the oxidation may vary from the slow decay of organic matter occupying may be centuries, to the rapid inflammation—explosion or detonation wave—travelling at the rate of 10,000 feet per second.

Pyrophoric powders—Finely divided lead is prepared by heating lead tartrate, at as low a temperature as possible, in a glass tube sealed at one end When the evolution of gas has ceased either close the open end with a cork, or seal it up hermetically while hot. If the cold powder be allowed to fall through the air on to the floor, the oxidation of the powder proceeds so rapidly that the temperature is raised and the falling powder becomes red hot [1] Hence the term *pyrophoric lead* Finely divided iron oxalate, nickel oxide, etc, reduced at a low temperature in a stream of hydrogen, also furnish pyrophoric powders

Spontaneous combustion—The so called spontaneous ignition of coal which takes place in gob,[2] in coal stacks, in coal bunkers, etc, may be caused by the oxidation of pyrites in the coal, or the coal itself,[3] owing to excessive ventilation leading to a more rapid supply of air Heat is generated In some cases, if ventilation be defective, the heat is not dissipated, but warms up the mass, the speed of oxidation is accelerated by the rise in temperature, this generates still more heat until finally the mass ignites Some coal dust mixed with air ignites in the vicinity of 200°

Oxidation of oils—Many oils—linseed oil, nut oil, poppy oil, hemp oil—absorb oxygen. Linseed oil used for paint, for instance, absorbs oxygen and forms a tough resinous skin as the paint "dries" This skin holds the colouring matters in suspension and protects the material underneath. The paint oils, therefore, do not "dry," in the ordinary sense of the word, by evaporation, but by oxidation The heat generated during the oxidation is dissipated, but if rags, etc, greasy with oil, be left in a badly ventilated place, or if a heap of greasy material be left for some time undisturbed under such conditions that the mass is not well enough

[1] The experiment is more amusing if the powder be allowed to fall on a *small* heap of gunpowder

[2] "Gob" is the space from which coal has been removed, and where the slack' is usually left behind as worthless

[3] There are other causes of underground fires

ventilated to keep it cool, the temperature may rise high enough for spontaneous inflammation The oxidation of the paint oils is facilitated by the addition of lead and manganese salts.

Eremacausis —The decay of wood is a process of oxidation, very slow, it is true, and it proceeds by what appears to be a roundabout process The end products, however, so far as we can tell, are the same as those obtained by direct combustion The heat of the reaction too is no doubt the same (Hess' law) whether the wood decomposes slowly with the formation of a large variety of intermediate products, and after a number of years ending in carbon dioxide and water, or whether it proceeds more directly in a few minutes by combustion In both cases the same amount of energy is degraded although the process of degradation proceeds by different reactions The process of slow oxidation without the application of heat is sometimes called slow combustion or eremacausis—from the Greek ἠρέμα (erema), quietly, καῦσις (causis), to burn The rusting of iron (*q v*) is another example of a slow oxidation, although the end product is not the same as in the combustion of iron in oxygen In the former case a hydrated ferric oxide—$Fe_2O_3\,nH_2O$—is formed, and in the latter case magnetic iron oxide—Fe_3O_4 The absorption of oxygen by rusting iron is generally illustrated by inserting a plug of steel wool, *A*, Fig 263, into a 100 c c eudiometer tube *B*, resting in a dish of water *C* The level of the water *B* is adjusted, and the apparatus examined after about twenty-four hours The iron will be coated with rust, and the enclosed air will have decreased in volume A stick of phosphorus at the end of a wire may be held in the cylinder in place of the iron The result of the experiment will be similar—removal of oxygen

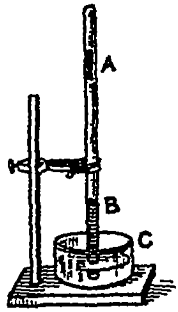


Fig 263 —Iron Rusting

In the "dilution method" of sewage treatment, the sewage is mixed with a large volume of water The oxygen dissolved by the water, assisted by bacteria, quickly renders the organic matter innocuous mainly by oxidizing it into carbon dioxide and water—and possibly nitrogen compounds

§ 4 Respiration involves Oxidation

John Mayow (1674) demonstrated that the respiration of animals is a process of oxidation analogous with combustion Mayow placed a mouse in a cage under a vessel standing over water—Fig 264—and noticed that the water rose in the jar as respiration continued just as if a burning candle had been placed under the jar—p 733, owing to the withdrawal of "nitroaërial particles" (oxygen) He found that the mouse died after a time, and it was impossible to ignite a combustible body in the residual "aërial" gas (nitrogen)

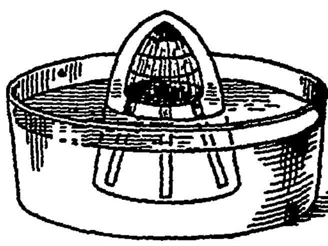


Fig 264—Mayow's Experiment on Respiration

Metabolism of animals and plants — All living organisms are continually wasting tissue as a result of muscular or other forms of

work.[1] The air during respiration loses about 4 to 5 per cent of oxygen, and gains 3 to 4 per cent of carbon dioxide Oxygen, taken in by the lungs, is absorbed by the blood. The blood contains hæmoglobin, this unites with oxygen, forming oxyhæmoglobin—the former is present in blue venous blood, the latter, in red arterial blood. The oxyhæmoglobin gives up to its oxygen very readily, and it thus oxidizes the waste products—partly to carbon dioxide The carbon dioxide held in solution by the venous blood is pumped by the heart to the lungs, and the gas is finally exhaled in the breath

By breathing into a beaker, and then adding clear lime-water, or better, by blowing through a glass tube into a beaker containing clear lime-water, it is easy to demonstrate the presence of carbon dioxide in the breath The precipitation of calcium carbonate causes the clear lime water to become turbid, etc The experiment can be modified by drawing a stream of air through pieces of "soda-lime" in a tower, *A*, Fig 265, to remove carbon dioxide from the air, then through a washbottle, *B*, with clear lime water The clarity of the lime water demonstrates the absence of carbon dioxide in the stream of air The air after passing the *temoin* (witness) tube, *B*, enters a glass chamber, *C*, which holds a mouse or a couple of mice, and then passes through another washbottle, *D*, containing clear lime water The turbidity of the lime water in *D*, and the clarity of the lime water in *C*, can only be explained by assuming that the mice are giving off carbon dioxide during respiration. The same vessel *C* can be used for trying the effect of different gases on mice

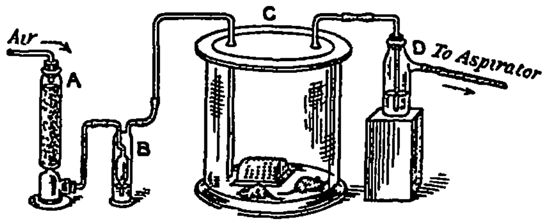


FIG 265 —Exhalation of Carbon Dioxide by Animals

Less carbon dioxide is exhaled during sleep because less waste products are formed. The heat evolved during the oxidation processes in the body maintains the body at the necessary temperature In the case of plants, most of this work is done by the leaves. The respiration of animals and plants goes on continuously, night and day—oxygen (air) is taken in, and returned to the air as carbon dioxide and water The consequent loss in weight in both animals and plants is made good by assimilation or feeding Fish abstract dissolved oxygen from water by the aid of their gills Fish quickly die for want of oxygen when placed in cold water which has been deprived of dissolved "air" by boiling Aerated water[2] furnishes the oxygen necessary for their sustenance

Assimilation by plants —The respiration of plants must not be confused with the process of assimilation. In daylight, plants absorb carbon dioxide from the air, fix the carbon, and give off oxygen In sunlight,

[1] Those constructive processes by which substances taken in as food by living organisms are converted into protoplasm and their own proper substance, are said to be anabolic—from the Greek ανα (ana), anew, βαλλειν (ballein), to throw Those destructive processes by which the protoplasm, etc, breaks down into simpler products are termed katabolic—from the Greek κατα (kata), down The two phenomena are included under the term metabolism—Greek μετα (meta), about.

[2] That is, water containing dissolved oxygen, or rather air

the process is very active so that the respiration process, though at work, is masked because more carbon dioxide is taken in and oxygen given out by assimilation (feeding), than oxygen is taken in and carbon dioxide given out by respiration (breathing) The decomposition of the carbon dioxide (feeding) only occurs in daylight, and plant life is thus dependent upon this process for nourishment This action of light may be readily shown by loosely packing a two litre flask with green leaves, and filling up the flask with water through which carbon dioxide has been allowed to bubble. Fit the flask with a stopper, and funnel as shown in the diagram, Fig 266. Also fill the flask and part of the funnel with water. A test-tube inverted over the funnel will collect sufficient oxygen to allow the usual tests being made [1]

The energy required for the decomposition of the carbon dioxide is derived mainly from the solar light and heat. There is thus a transformation of the sun's energy into chemical energy which is stored up is vegetable tissue. The heat of combustion of burning wood is believed to be equivalent to the solar energy used in its formation (Hess law) At night, in darkness, feeding stops but breathing—the absorption of oxygen and the evolution of carbon dioxide—continues The net result of both processes—assimilation and respiration—is to remove carbon dioxide from the air, and restore oxygen. There is probably a kind of equilibrium pressure between plants and the carbon dioxide of the air If the amount of carbon dioxide exceeds a certain limit, this would be followed by greater activity in vegetable life, and thus the normal proportion of carbon dioxide would be restored. Similarly, if the amount of carbon dioxide were reduced below the normal, vegetable life would be impoverished until equilibrium was restored. The proportion of carbon dioxide present in the gases dissolved by seawater is about 27 times as great as the proportion of this gas in air. Since carbon dioxide is very soluble in water, it follows that if a large surplus of carbon dioxide were introduced into the atmosphere, say, from volcanic sources, the sea would dissolve a still greater proportion Hence *the sea must be an important means of regulating the amount of carbon dioxide in the atmosphere*

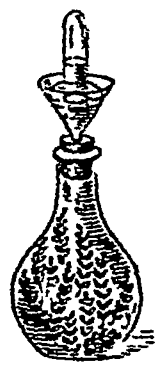


FIG 266 — Assimilation of Carbon Dioxide by Plants

It will be noticed that all animal and vegetable life is dependent upon the carbon dioxide → carbon reaction, which in turn is dependent upon the sun s energy There is a kind of closed cycle, an alternation of oxidations and deoxidations:

Sun's energy stored—plants feed

Energy dissipated—animals and plants breathe, etc

[1] If the water be too highly charged with carbon dioxide, it may be necessary to remove the carbon dioxide from the oxygen, before testing, by means of a

maintained by a continuous supply of energy from the sun. If the supply should cease, the deoxidation of carbon dioxide would stop and the present conditions of life on the earth would come to an end because the available carbon would be transformed into unavailable carbon dioxide

§ 5 Ignition Point, Kindling Temperature

We have seen that the speed of a chemical reaction is usually accelerated by raising the temperature, and also that in *exothermal reactions*, heat is evolved in consequence of the chemical action If finely divided phosphorus be exposed to the air, oxidation commences, heat is developed by chemical action more quickly than it is conducted away In consequence, there is a rise of temperature This accelerates the speed of oxidation and causes a still greater development of heat This, in turn, still further accelerates the speed of the reaction until, when the temperature has risen to about 60°, the phosphorus bursts into flame The **ignition or kindling temperature is the temperature to which the substance must be heated in order to start combustion or explosion** Phosphorus, at temperatures below its own ignition temperature, does not combine with oxygen fast enough to cause inflammation, at and above this temperature, the oxidation is attended by combustion Many substances inflame spontaneously at ordinary temperatures, for instance, phosphorus, boron and silicon hydrides, zinc ethyl, etc This means that the ignition temperatures of these substances are at or below ordinary atmospheric temperatures The ignition temperature must not be confused with the temperature of the reaction The ignition temperature is no more the temperature at which the reaction begins than the boiling point of water is the temperature at which evaporation begins

If the heat could be conducted away from the oxidizing phosphorus quickly enough, the temperature of the reacting substance would never reach the ignition point Substances in vigorous combustion, if cooled below the ignition temperature at the seat of the reaction, may be extinguished In illustration, a candle flame can be extinguished by placing a helix of copper wire about the flame, whereas, if the helix be first heated, the flame will not be extinguished.

It is not necessary to heat all the reacting system to the temperature of ignition The heat may be applied locally A lighted match applied at one point will ignite a barrel of gunpowder, and a small electric spark is sufficient to inflame a vessel of detonating gas But a sufficient quantity of the mixture must be ignited to develop enough heat to prevent its being conducted away so quickly that the temperature cannot be maintained above the ignition temperature when the stimulus is withdrawn Thus, sparks below 0 22 mm in length will not ignite electrolytic gas. The nitrogen and oxygen of atmospheric acid can be made to burn in an electric arc with a flame producing nitric and nitrous acids, but the evolution of heat is not sufficiently great to raise the temperature of the gas up to its ignition point If otherwise, the flame would quickly spread through the atmosphere, and "deluge the world in a sea of nitric and nitrous

little potassium hydroxide solution Leaves of the "Common Birdsfoot" were used in the apparatus, Fig 266

acids" (W Crookes) In endothermal reactions, too, the reaction may be started at one point, heat is absorbed from the surroundings, the temperature at the seat of the reaction is reduced, and the speed of the reaction slows down, until finally, the reaction comes to a standstill.

The ignition temperature of oils is an important subject where petroleum oils are used for illumination, cylinder oils in high pressure steam, etc Grave dangers attend the use of oils with too low an ignition temperature, or, to use the commercial term, too low a flash point The flash point of an oil is defined as "the temperature at which the oil gives off sufficient vapour to form a momentary flash when a small flame is brought near to surface" The apparatus shown in Fig 267 is a convenient way of performing the test A beaker is fitted with a cork having a hole in its centre. A thermometer and two electrodes are also fitted in the cork The tips of the electrodes are about 5 or 10 mm apart The beaker is fixed in a water-bath, the central hole in the cork is covered with a glass plate, the temperature of the bath is gradually raised, and sparks are sent across the wires by connecting the wires with an induction coil and accumulator, when the temperature reaches the flash point, the glass plate is lifted up by a small explosion The temperature indicated by the thermometer is the flash point of the oil Slightly different "flash points" are obtained by different methods of applying the test It has been found necessary to legislate against the use of kerosene, petroleum, etc, with a flash point below a certain prescribed temperature, which is not the same in different countries—44° C, or 111° F is about the average It is difficult to determine the exact ignition temperature of gases because the ignition temperature is conditioned by the temperature and pressure of the gas, the rate at which heat is conducted away from the seat of the reaction, etc Numbers varying from 500° to 845° have been published for the ignition point of electrolytic gas

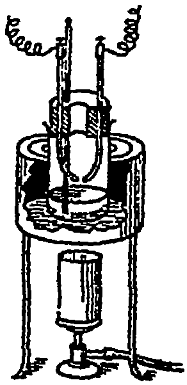


Fig 267 —Determination of Flash-point

§ 6 Explosions.

From the preceding section, it will appear that there is no real line of demarcation between rapid combustion and an explosive combustion The speed of the explosion is determined by the rate at which the process of combustion, initiated at one point, travels through the mixture Careful measurements indicate that the explosion of gaseous mixtures have this peculiarity the speed of explosive combustion increases rapidly from its point of origin until it has attained a maximum speed, after that, the explosion travels with the uniform maximum speed. The maximum speed has a specific value for each explosive mixture under definite conditions This constant is called the velocity of the explosion or detonation wave If a mixture of gases explodes under such conditions that the explosion wave is inaugurated, the explosion will be far more violent than if it occurred under such conditions that the explosion wave was not established The explosion wave, at top speed, travels

§ 7 The Safety Lamp Flame Caps

A stout glass tube *B*, Fig 269, about 3 cm diameter and 60 cm long, is fitted at one end *A* with a perforated rubber stopper and bent glass tube; the other end is fitted with a perforated stopper and copper tube *C* about 6 mm in diameter and 30 cm long The tube is clamped to make an angle of about 30° with the horizontal Fill the tube with coal gas by connecting *C* with the gas supply, light the gas at *C* and remove the stopper at *A* Air enters at *A* and makes an explosive mixture of air and gas in the tube. The flame at *C* will retreat down the *C* tube and explode the gas in *B*. Repeat the experiment using a copper tube 3 mm in diameter at *C* The flame will be extinguished in *C* before it reaches the gas in *B*[1] That *B* does contain an explosive mixture of air and gas can be shown by applying a lighted taper at *A* Consequently the flame is cooled below the ignition temperature of the mixture, during its passage down the narrower copper tube, but not with the wider copper tube

Again, fix a piece of wire gauze over an unlighted Bunsen's burner, turn on the gas, bring a lighted taper above the gauze, the gas above the

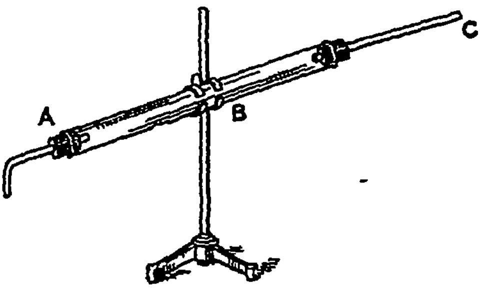


Fig 269 —Gas Explosion

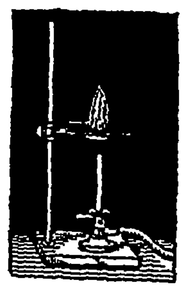


Fig 270 —Effect of Wire Gauze on Flame

gauze is ignited, but the flame does not pass through the gauze, Fig. 270 Conversely, if the gas be ignited below the gauze, the flame will not pass through, although the passage of inflammable gas through the gauze can be demonstrated by bringing a lighted taper above the gauze If the gauze be heated red hot, the flame will pass through and burn on both sides

Experiments not unlike these, led Humphry Davy, in 1815, to the idea of "flame sieves," and finally to the "safety lamp for miners" In Davy's safety lamp, Fig 271, an oil lamp is surrounded by a cylinder—1¼ inches in diameter, and 6 inches high—made of iron wire gauze, having 28 meshes per linear inch The cylinder is closed at the top with a double layer of gauze *A*, Fig 271 The lamp is provided with a screw lock to prevent it being opened in the mine, and there is a ring at the top to allow the lamp to be carried or suspended. The lamp is ventilated by air passing through the mesh of the gauze near the flame The air impinges on the flame, and the products of combustion escape through the gauze in the upper part of the cylinder When such a lamp is taken into an atmosphere containing a mixture of marsh gas and air, the explosive mixture passes through the gauze and is ignited inside the cylinder The cylinder may (but

[1] A little adjustment is needed in getting the right angle for a successful experiment

should not) be heated red hot by the combustion of the explosive gases inside The flame, however, is unable to pass through the gauze and ignite the mixture outside the cylinder The gauze acts as a "flame sieve", it permits a free passage of gas, air, and light, but it obstructs the passage of the flame Prior to the invention of Davy's lamp, the risk of explosion in "fiery mines" was very serious The Davy lamp considerably lessened the danger Mr Buddle, one of the first users of Davy's lamp, in a Report on Accidents in Mines (1835), stated *inter alia*

> I first tried it in an explosive mixture on the surface, and then took it into a mine; and, to my astonishment and delight, it is impossible for me to express my feelings at the time when I first suspended the lamp in the mine and saw it red hot, if it had been a monster destroyed, I could not have felt more exultation than I did

If the gauze should happen to be heated locally above the ignition temperature of the mixture outside, or if the lamp is exposed in a strong current of air, say a ventilating shaft, or a "wave" of air sometimes generated in the operations of blasting, the flame may be driven through the meshes of the gauze Considerable improvements have been made on the original *Davy's lamp*, *A*, Fig 271 The modern forms of safety lamp—*e g J B Marsaut's lamp*, *B*, Fig 271—allow the lamp to be used under conditions of great danger with a minimum risk of igniting an explosive mixture of firedamp and air The old Davy's safety lamp is obsolete It gives a very poor illumination owing to the obstruction offered by the wire gauze, and the flame may be forced through the gauze when the current of air exceeds 5 feet per second, and in modern mines, the air in some parts of the rapid ventilating roads may attain 20 to 30 feet per second

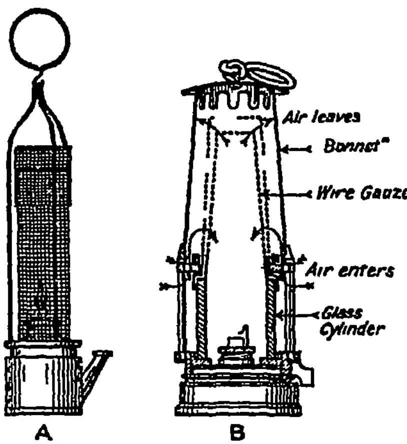


FIG 271 —Safety Lamps (old and new)

The appearance of the flame of the safety lamp depends upon the illuminant and on the amount of firedamp present in the atmosphere of the mine The first noticeable effect of firedamp is a slight flickering or "jumping" of the flame, as the amount of firedamp increases, the flame becomes more and more elongated and smoky until it stretches upwards to the gauze of the lamp as a long thin smoking column The flame may then leave the wick and burn in the upper part of the gauze with a faint bluish light—called by the miners "corpse light", or the flame may be extinguished.

The peculiar appearance of the flame is due to the formation of an aureole, or flame-cap of burning firedamp which surrounds the flame proper The flame cap is transparent and non luminous by contrast with the bright flame of the lamp itself To make it visible, the flame, burning from a well-trimmed wick, is "pulled down" as low as possible until a clear blue aureole entirely surrounds a small luminous yellow spot of light, and

the flame extends right across the wick This may be called the standard flame E B. Whalley and W M. Tweedie (1910) found that with "white rose" paraffin oil, the first indications of firedamp occur when about one per cent of the gas is present A very faint cap, without visible tip is then just visible, with two per cent of firedamp the tip of the cap is just visible, and the cap has increased in length, the length increases slowly when between 2 and 3 per cent of firedamp is present, the increase in length is rapid between 3 and 4 per cent of firedamp, and still more rapid between 4 and 5 per cent when the flame "spires" up to the

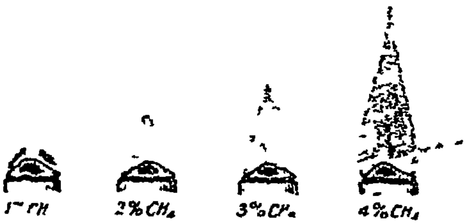


FIG 272 —Flame caps—Whalley and Tweedie

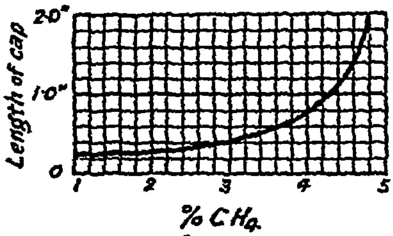


FIG 273 —Effect of Methane on Length of Flame caps—Whalley and Tweedie

top of the gauze The appearance of the aureole or flame-cap with these different amounts of firedamp is indicated in Fig 272, and a graph of the experimental results in Fig 273 It is now possible to form a very fair estimate of the amount of marsh gas in the mine air from the elongation of the flame by using illuminants, etc, standardized in atmospheres containing definite proportion of marsh gas The method is daily used in coal mines for detecting dangerous amounts of firedamp

§ 8 The Relation between the Combustible and the Supporter of Combustion

It has been found convenient in our previous studies to call the burning substance the combustible, and the atmosphere surrounding the burning substance the supporter of combustion Under ordinary conditions the atmosphere is the enveloping medium, and the terms "combustible" and "incombustible," without further amplification, refer to the burning or non-burning of substances in air Conventionally too, other gases are said to be supporters or non-supporters of combustion if they behave towards ordinary combustibles like air These terms, however, are purely conventional because, from the chemical point of view, it is a matter of indifference whether coal gas burns in air, or air in coal gas If the atmosphere be coal gas, the flame must be fed with atmospheric air In this case, the meaning of the conventional terms is reversed, for air is then the combustible, and coal gas the supporter of combustion There are several ways of showing this reversed or reciprocal combustion, as it is called.

An ordinary lamp cylinder—*A*, Fig 274—may be closed at one end with a cork perforated to fit over a Bunsen's burner,[1] *B*, and also with a

[1] Or with a glass tube connected with a Bunsen s burner

hole in which a glass tube *C*—about 10 cm. long and 1 cm diameter is fitted. The top of the cylinder is covered with a sheet of asbestos *D*—6 or 7 cm square, and perforated with a round hole about 2 cm. diameter The air holes of the Bunsen's burner are closed, the gas is turned on and the opening in the asbestos is closed by laying a piece of cardboard loosely on the hole In a few minutes, the apparatus will be filled with coal gas. Light the gas as it issues from *C*, and simultaneously remove the cardboard which was closing the hole in the asbestos The flame will pass up the tube drawing the air after it The upward current of gas causes an upward current of air in the tube *C* which burns with a feebly luminous flame in the atmosphere of coal gas The excess of coal gas issuing from the opening in the asbestos may be ignited, and the two flames show air burning in coal gas, and coal gas burning in air By modifying the arrangement, Fig 274, it is easy to show hydrogen and marsh gas supporters of combustion, and oxygen, chlorine, and nitrous oxide as combustibles.

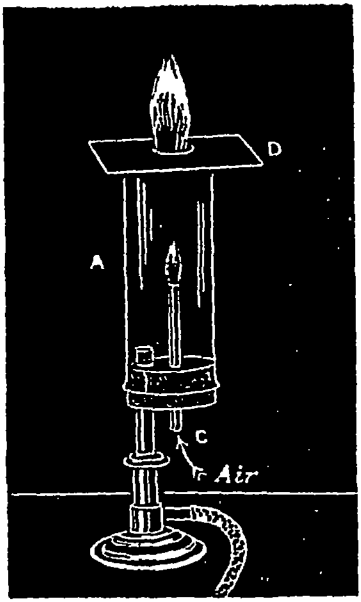


Fig 274—Reciprocal Combustion

§ 9 The Structure of Flame

The development of flame during combustion is quite an accidental feature Iron burning in oxygen gives no perceptible flame The intense light is due to the incandescent solid. Similar remarks apply generally to the combustion of solids which are not volatilized at the temperature developed during combustion For this reason, also, copper, carbon,[1] etc, do not usually show any appreciable flame On the other hand, phosphorus, sulphur, bitumen, fat, wax, etc., burn with a flame because these solids are volatilized at the temperature of combustion

The flame of most of the combustible gases has quite a characteristic appearance—sulphur burns in air with a lavender blue flame, burning hydrogen is scarcely visible in bright daylight, provided the gas and air are free from dust, carbon monoxide has a rich blue flame, silicon hydride a pale green flame, the cyanogen flame has a delicate pink tinge, acetylene burns with a highly luminous yellowish flame, while marsh gas burns with a feebly luminous yellowish flame

It will be obvious that when a stream of gas issues from a tube, the gas can only burn at its surface of contact with the air The shape of the flame, issuing from, say, a circular jet, is due to the fact that as the gas issues from the jet, a ring of gas, so to speak, next to the tube burns first, before any more gas can come in contact with the air and burn, it must

[1] If carbon burns to carbon monoxide, and then to dioxide, flame may be produced by the burning carbon monoxide

rise past the first ring of flame, and each successive layer of gas has to pass higher and higher before it can find the supply of air necessary for combustion The flame thus assumes the form of a cone Of course there are no real "rings of gas," but this mode of expression helps us to understand the phenomenon The upward direction of the flame, even if the gas be directed horizontally or downwards is due to the increased buoyancy of the hot air in immediate contact with the flame producing a strong upward current of air The particular shape of the flame is also conditioned by the pressure behind the gas issuing from the tube, and on the character of the jet—*e.g* the so called "bat's-wings," and "fish-tail" burners

The interior of the flame which does not come in contact with the air is unburnt gas Numerous experiments have been devised to show this For instance

(1) Cross sections of the flame can be shown by depressing thin sheets of asbestos paper (say, 15 cm square) for a few moments on the flame of, say, a Bunsen's burner protected from draughts The hotter portions of the flame where the gases are burning char the paper [1] producing a dark ring when the paper is held horizontally, Fig 275, *B*, and a more or less elongated cone if the paper be held vertically in the flame *A*, Fig 275 The particular "flame figure" produced depends on the part of the flame in which the paper is held N Teclu (1891)

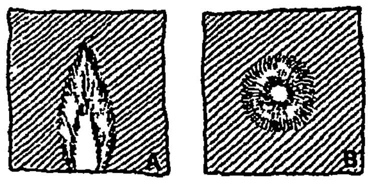


Fig 275 —Flame Figures

(2) A narrow glass tube—say 20–30 cm long—held in the centre of the flame will draw off a portion of the unburnt gas from the interior, and the unburnt gas can be lighted at the end of the tube—Fig 276

(3) A pin pushed at right angles through the stem of a match about 3 cm from the tip, enables the tip of the match to be supported about 3 cm above the jet of, say, a Bunsen's burner The gas can be lighted The match will remain in the centre of the flame without inflaming The experiment can be modified by thrusting the match into the centre of the flame as illustrated in Fig 277

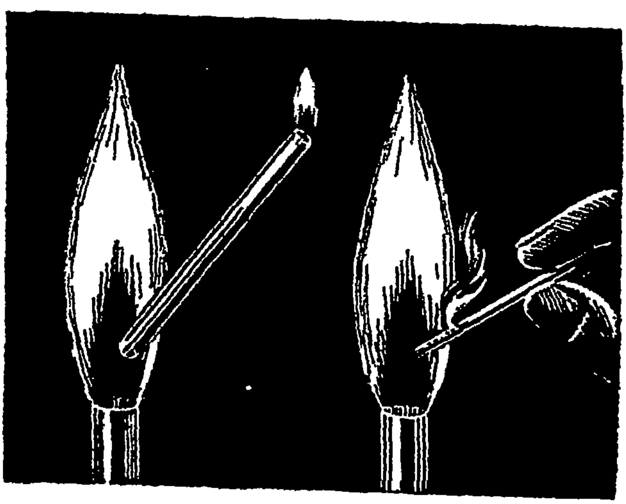


Fig 276 Fig 277
Flame Experiments

(4) The preceding experiment can be modified by connecting a 5–7 cm funnel with the gas supply as illustrated in Fig 278 The broad mouth of the funnel is covered with a piece of fine copper or brass wire gauze A small conical heap of gunpowder (1½ cm base) is placed on the middle of

[1] Grease or oil is used in making the asbestos paper Well glazed white writing paper can also be used The upper side of the paper can also be dusted with red mercuric iodide This turns yellow where the flame is hottest Copper foil also furnishes an interesting modification of the experiment

the gauze[1] The gas is turned on, and a lighted taper slowly depressed from above downwards to the funnel until the gas is ignited The gunpowder remains on the gauze unconsumed Ordinary matches can be thrust through the flame and laid on the heap of gunpowder without being ignited

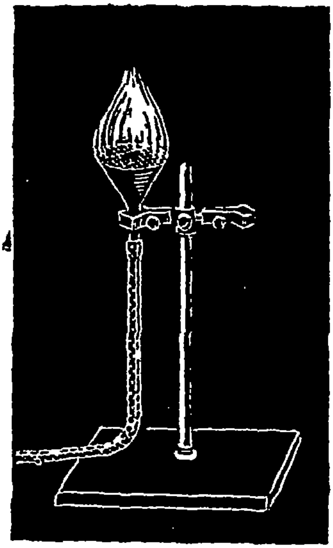


FIG 278 —Hollowness of Flame

Single mantled flames —The nature of the chemical actions which occur in the flame during the burning of gases like hydrogen in air and in chlorine are probably much simpler than is the case with gases like methane, ethylene, and acetylene, for the latter form complex decomposition products This is evidenced to some extent by the structure of the hydrogen flame In the former case, the flame is a cone with a uniform sheath of the burning gas as is illustrated in Fig 279 The interior cone contains unburnt gas

Double mantled flames —The flame of cyanogen has an inner rose coloured mantle with an outer bluish sheath The carbon is oxidized to carbon monoxide in the inner mantle, and to carbon dioxide in the outer mantle The nitrogen remains practically unoxidized. The flame of hydrogen sulphide in air consists of the usual inner cone surrounded by a lilac coloured mantle which in turn is surrounded by a mantle of deeper blue The hydrogen sulphide is probably decomposed in the inner part

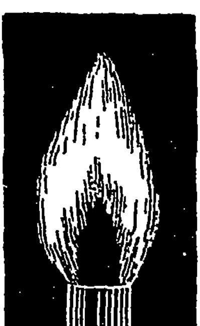


FIG 279 —Hydrogen Flame

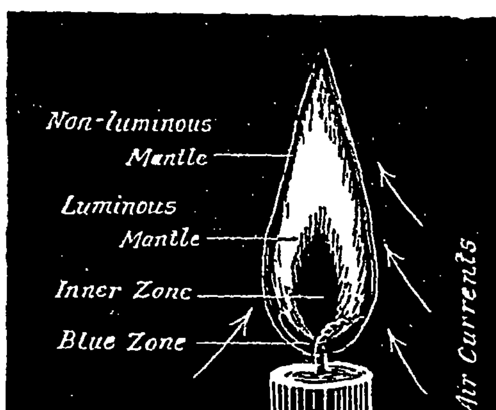


FIG 280 —Candle Flame

of the flame and immediately burns in the mantles to sulphur dioxide and water The ammonia flame in oxygen is somewhat similar to the cyanogen flame—the inner mantle is ochre yellow, and the outer mantle

[1] Gunpowder must not be placed on the hot wire gauze, and it must be kept in a compact heap so that no particles are scattered about

is pale yellow tinged with green Carbon disulphide resembles hydrogen sulphide, but the carbon burns to carbon dioxide With carbon disulphide and hydrogen sulphide both constituents are combustible, with ammonia and cyanogen only one constituent is combustible although a trace of the nitrogen may be oxidized.

Burning hydrocarbon gases, burning candles, and burning oils also furnish double sheathed flames—Figs 280, 281 The inner mantle is bright yellow, more or less opaque and luminous, the outer mantle is but faintly luminous In addition, there is a bluish non-luminous zone of incomplete combustion at the base of the flame With the flame of oil lamps and candles, the hydrocarbons are drawn up the wick by capillary action and vaporized near the top of the wick, in the case of a candle, the wax is

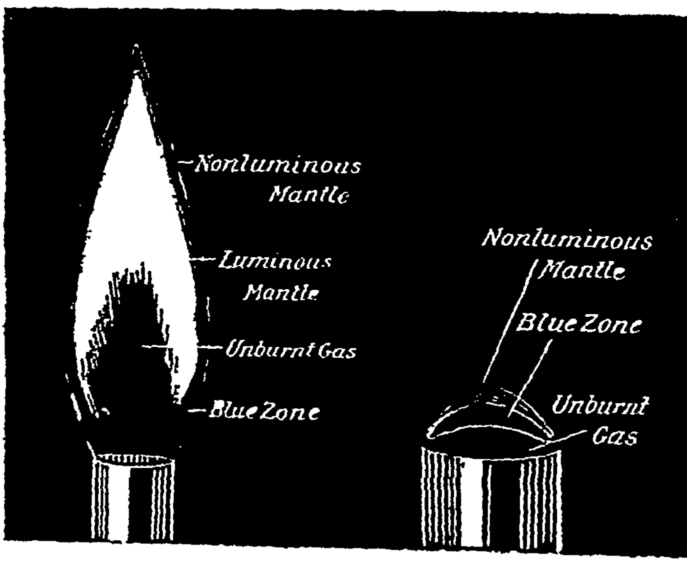


FIG 281 FIG 282
Flames of Coal Gas

melted by the heat of the flame The wick is so plaited that it curls over and exposes the tip to the air The tip of the wick is thus gradually burnt, and "snuffing" is not needed.[1]

When the flame of gas is gradually lowered, the inner luminous sheath gradually decreases in size, and finally disappears, at the same time, the blue region of incomplete combustion at the base becomes continuous right across the flame, Fig 282 It is probable that the blue portion represents unburnt gas Between the flame and the burner there is a space containing unburnt gas The small central cone also contains unburnt gas

Smithells' flame separator—A Smithells has designed an apparatus (1891) which illustrates in an interesting manner the presence of the two mantles in an ordinary coal gas flame The apparatus consists

[1] If the wick does not curl, it is liable to project into the inner cone of the flame as the wax is consumed, and thus interfere with the proper combustion of the candle

of two co axial tubes A and B, Fig 283 The outer wider tube is shorter than the inner tube and fitted with a rubber union C, and a brass clip to permit the outer tube to be slid up and down The upper ends of the co axial tubes are fitted one with a mica D and the other with an aluminium E cylinder The narrower tube is clamped over an unlighted Bunsen's burner and a loose packing of cotton wool F placed between the burner and the glass tube Adjust the tops of the co axial tubes at the same level Close the air holes of the Bunsen's burner, turn on the gas, light the gas at the top of the outer tube The gas burns with the usual luminous coal gas flame Gradually open the air holes of the burner until the flame appears non-luminous Slide the outer tube upwards, and the two coned structure of the flame will be obvious, for the outer cone ascends with the wide tube, while the inner cone, after the tube has been pushed upwards about 10 cm, remains burning at the top of the inner tube.

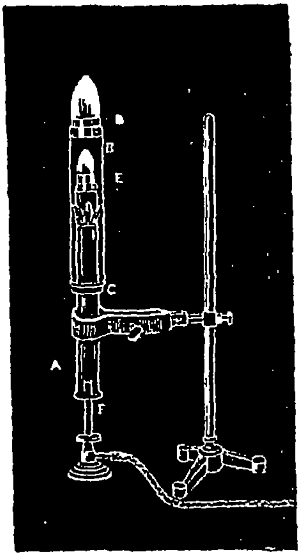


Fig 283 —Smithells' Experiment

§ 10 The Nature of the Chemical Reactions in Flames

The chemical reactions which occur in the flames of burning hydrocarbons have not been satisfactorily elucidated, although a little is known Tapping the gases from different parts of the flame by means of platinum or porcelain tubes connected with an aspirator, is not very satisfactory, because of the changed conditions arising when the reactions take place in contact with solids Hence, the proof that the flame of burning hydrogen sulphide contains free sulphur, and that the luminous mantle of burning hydrocarbons contains free carbon, because a cold dish held in the flame receives a deposit of the respective solids, is quite unsatisfactory It is conceivable that the hydrogen sulphide flame contains free sulphur, and the hydrocarbon flame free carbon when cold porcelain is held in these flames, but not when this disturbing agent is absent, we therefore prefer demonstrations with methods which do not interfere with the flame itself

1 *The inner cone* —If the flame of coal gas, or of a candle be placed between a strong light and a screen, the luminous portion of the flame throws a dark shadow on the screen, and if the flame be made to smoke, the shadow of the luminous portion extends into the shadow cast by the smoke This test for solid matter in flames is called J L Soret's optical test (1875), and is generally taken to prove that free carbon is present in the luminous portion of the flame of a hydrocarbon gas because the flame in the non-luminous portion gives no shadow, nor do the flames of carbon disulphide, phosphorus, and other gases which are known to contain no solid matter The temperature of the inner cone of unburnt gas is raised by heat radiated from the surrounding mantles of burning gas It is known that when certain hydrocarbon gases are heated in the absence of air, free carbon

and dense hydrocarbons are formed [1] Acetylene, for instance, is formed This can be shown by burning air in coal gas (Fig 284), so that the ordinary flame is turned inside out, so to speak, when the acetylene, now on the outer surface of the flame, is readily drawn off into the atmosphere of coal gas, and afterwards precipitated by passing the gases through a solution of cuprous chloride (p 697), as illustrated in Fig 284

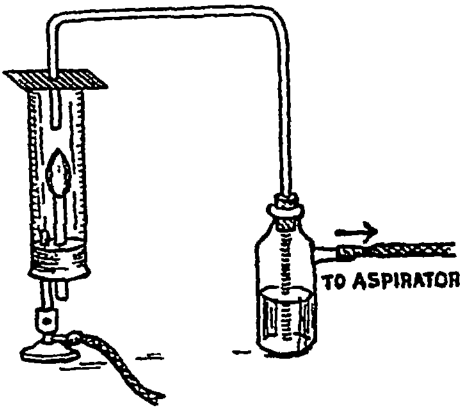


Fig 284 —Acetylene in Coal Gas Flame

If the flame be chilled, there is a considerable diminution in the luminosity, so much so that the flame becomes practically non-luminous This is well illustrated by holding a piece of sheet nickel or iron against a small flame of coal gas burning from a fish-tail burner (Fig 285) If the opposite side of the sheet of nickel be heated by means of a blowpipe or large burner, the luminosity of the flame will be restored On the other hand, if the gas or air be heated, a non-luminous flame becomes distinctly luminous This can be illustrated by fixing a 15 to 20 cm tube made of platinum foil over the end of an ordinary Bunsen's burner so as to extend the main tube (Fig 286) When the platinum tube [2] is

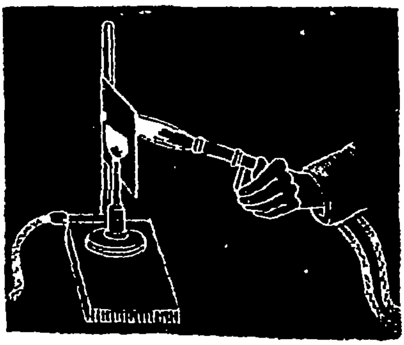


Fig 285

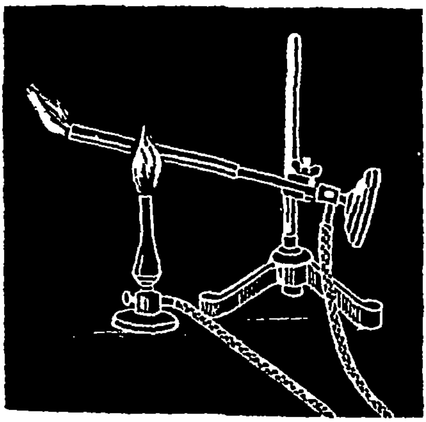


Fig 286

Luminosity of Flames

heated by the flame of another burner, the non-luminous Bunsen's flame becomes distinctly luminous Similarly, diluting the coal gas with an

[1] According to V B Lewes (1895) at temperatures between 800° and 1000° part of the ethylene decomposes into acetylene and methane $3C_2H_4 = 2C_2H_2 + 2CH_4$ along with other more complex hydrocarbons—naphthalene and benzene Above 1200°, methane, ethylene, acetylene, are decomposed into carbon and hydrogen

[2] The platinum tube should be heated before the test is made to burn off the dust, volatilize the sodium chloride, etc

inert gas like carbon dioxide leads to a loss in illuminating power Thus, one of the air holes at the base of a Bunsen's burner may be closed by a cork. and the other fitted with a glass tube connected with a Kipp's apparatus, *K*, generating carbon dioxide, and a drying tube *C* (Fig 287) By gradually increasing the amount of carbon dioxide, the luminosity of the flame can be reduced until it finally becomes blue If the diluting gas be heated, by heating the tube, *B*, the luminosity of the flame is restored. This all seems as if the high temperature flame favours the decomposition of the hydrocarbons in the inner cone into free carbon, etc , and that the free carbon adds to the luminosity of the flame [1] Hence it is assumed that *in the innermost cone the unburnt hydrocarbons are partly decomposed, at the high temperature of the inner mantle, into free carbon, acetylene, and other hydrocarbons*

2 The inner mantle —The result of the analysis of gases in this zone shows that carbon monoxide, hydrogen, carbon dioxide, and water

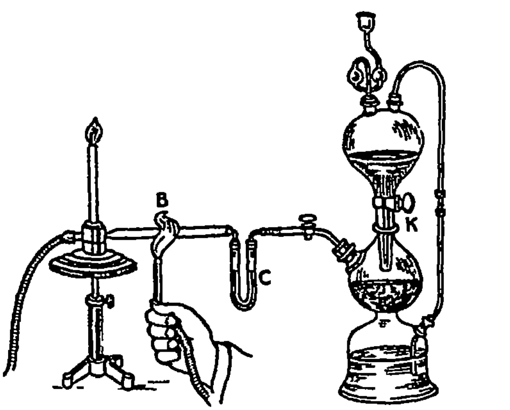


Fig 287 —Luminosity of Flames.

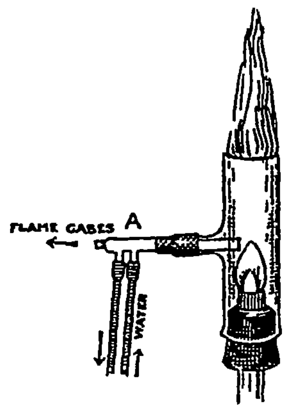


Fig 288 —Haber's Flame Experiment

are present [2] The little oxygen which can penetrate to the vicinity of the innermost cone oxidizes the hydrocarbons in such a way that carbon monoxide and hydrogen gases still remain unburnt. The idea can be gathered from the equations

$$C_2H_4 + O_2 = 2CO + 2H_2, \text{ and } C_2H_2 + O_2 = 2CO + H_2$$

No free oxygen has been detected in this part of the flame That which does penetrate into this region is used in oxidizing the two unburnt gases The oxygen distributes itself so that the gases carbon monoxide, water, hydrogen, and carbon dioxide are in equilibrium (see p 713)

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

When this deduction was tested experimentally by F Haber, the gases were drawn from the space between the inner and outer mantles of the

[1] The flame of coal gas burning in oxygen is much reduced in size, the luminosity is increased, and there is not sufficient carbon present to show an appreciable shadow

[2] Also nitrogen, of course. This is derived from the atmospheric air Every one volume of oxygen, it will be remembered, is accompanied by four volumes of nitrogen

flames of coal gas burning in a Smithells' flame separator fitted with a side tubulure connected with a double-walled water-cooled platinum tube, *A* (Fig 288) Hence, whatever view be taken of the nature of the chemical process in the inner mantle, the net result of the reactions leads to the conclusion *In the inner mantle, the hydrocarbons are oxidized to carbon monoxide and hydrogen gases, and these gases are in equilibrium with the carbon dioxide and water, formed at the same time. The relative amount of each gas present is determined by the temperature*

It was once taught by M Faraday (1853) and others that when a gas like ethylene—C_2H_4—is burnt, the hydrogen burns first and the carbon afterwards As H B Dixon has expressed the idea "There is a race for the oxygen of the air between the two constituents of ethylene, and the hydrogen being the fleeter of the two, gets to the oxygen first and is burnt to water" H. B Dixon (1893), W A Bone and J C Cain (1897), and C M Kersten (1861) have verified the old observation of J Dalton (1810) that when a mixture of acetylene or ethylene is detonated with insufficient oxygen to burn all the hydrogen and carbon, carbon monoxide and hydrogen are formed, roughly according to the equation $C_2H_4 + O_2 = 2CO + 2H_2$, and $C_2H_2 + O_2 = 2CO + H_2$ This certainly makes it appear that the carbon burns to carbon monoxide before the hydrogen Hence the idea of a selective or preferential combustion It seems as if nearly all the carbon is first oxidized to carbon monoxide, and the excess of oxygen, if any, divides itself between the carbon monoxide and hydrogen as indicated above.

It is not yet quite clear what really does take place at the temperature of the hydrocarbon flame There are many reasons for assuming that at rather lower temperatures, the oxidation takes place in a series of "steps" without any liberation of free carbon or free hydrogen at any stage of the process W A Bone heated a mixture of different hydrocarbons with oxygen at a temperature such that neither carbon monoxide nor hydrogen were oxidized with appreciable velocity, nor the steam reduced by carbon The experiment was arranged so that the gases were circulated alternately through a hot zone and through a washing apparatus for removing condensible or soluble intermediate products of oxidation The results showed that the oxidation is a complex process One example will suffice. According to Bone, the oxidation of ethylene probably takes place in the series of stages represented by the following equations

$$2C_2H_4 + O_2 \rightarrow \underset{\text{Vinyl alcohol}}{2C_2H_3OH} \rightarrow \underset{\text{Formaldehyde}}{4H\,CHO}$$

$$2H\,CHO + O_2 \rightarrow \underset{\text{Formic acid}}{2H.COOH} \rightarrow 2CO + 2H_2O$$

$$2H\,COOH + O_2 \rightarrow 2CO_2 + 2H_2O$$

$$2CO + O_2 \rightarrow 2CO_2$$

because all but the vinyl alcohol have been detected among the products of the oxidation The initial and end stages of the reaction are represented $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$ As indicated when discussing slow oxidation, it is highly probable that during the oxidation of hydrocarbons, and related materials in slow "natural" decay, p 737, a very complex series of "humic" compounds are formed before the final products—carbon dioxide and water—appear, the experiments of Bone on oxidations at rather higher temperatures, leads us to suppose that the reactions are somewhat simpler, and at the still higher temperature of the flame, the reactions are, in all probability, simpler still

3 The outer mantle —If everything be properly adjusted there is ample oxygen in contact with the outer mantle to oxidize all the carbon monoxide and hydrogen formed in the inner mantle $2CO + O_2 = 2CO_2$, and $2H_2 + O_2 = 2H_2O$ This part of the flame is chilled by the surrounding air If the gas issues from a jet at an excessive pressure, the air may not have time to oxidize all the carbon (smoke), hydrogen, carbon monoxide, and hydrocarbons. The gases, in consequence, are cooled before oxidation in the outer mantle is completed. Indeed, it is difficult to ensure complete oxidation because the cold air in contact with the flame lowers the temperature of the gases so quickly that a little hydrogen and carbon monoxide sometimes escape oxidation, and hence, traces of these gases are often found among the products of combustion With a properly adjusted flame, *in the outer mantle, the carbon monoxide and hydrogen formed in the inner mantle are completely oxidized respectively to carbon dioxide and water*

§ 11 The Luminosity of Flames.

A general explanation of the cause of the luminosity of flames is not known Pure hydrogen burning in dust-free air is almost invisible even in a dark room The hydrogen flame becomes luminous if the gas be passed through a tube containing a plug of cotton wool saturated with benzene The experiment is usually made by connecting a U tube with the tube delivering the hydrogen In Fig 289 the hydrogen is delivered by a Kipp s apparatus, and the gas is dried in a tower of calcium chloride, *C*

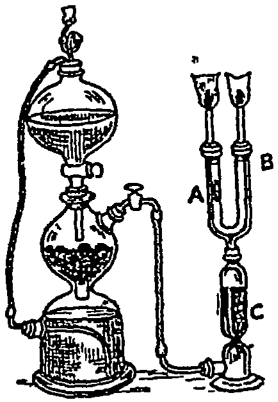


Fig 289

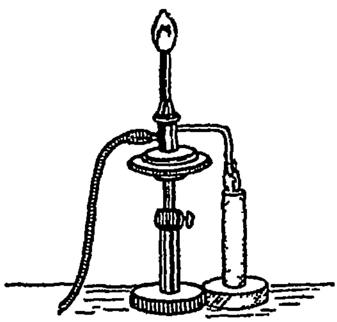


Fig 290

One leg, *A*, of the U tube has the plug of cotton wool Both legs of the U tube are fitted with jets—preferably fish-tail tips When all the air is expelled from both legs of the U tube, light the gas at both jets The characteristic hydrogen flame appears on one leg, and the luminous " carburetted flame " on the other leg A non-luminous Bunsen's flame can be made luminous by passing particles of carbon through the flame, say, by rubbing two pieces of charcoal together near the air holes of the Bunsen's burner, or by causing the air which passes through the air holes to pass over finely divided carbon—say lampblack from turpentine, or the hydrocarbon gases from a burning candle (Fig 290) can be tapped and

led into one of the air holes of the Bunsen's burner adjusted to burn with a non-luminous flame When the hydrocarbons are passing through the flame, the flame is luminous If alcohol is boiled in a flask and the vapour ignited at the mouth of the flask, a pale blue flame is obtained. If a jet of chlorine gas be passed through the flame, into the flask, the chlorine gas is ignited, and it burns with a luminous flame (Fig 291) The particles of carbon which separate rise into the alcohol flame and make it luminous.

Incandescent mantles—In Welsbach's burner, the flame is non-luminous like an ordinary Bunsen's burner. The Welsbach's mantle is hung so that it is heated by the burning gas The mantle becomes incandescent The mantle is made by saturating woven cotton fabrics with a mixture of, say, 99 per cent thoria and 1 per cent ceria The mixed nitrates are dissolved in water. The cotton fabric retains some of the salts in its pores The cotton is then allowed to dry and burnt off in a stove, at the same time, the nitrates are transformed into oxides The mantle is hardened and shaped in the blowpipe flame, and the result is a kind of fragile pottery which retains the form and shape of the original fabric It would be too fragile for transit It is therefore dipped in collodion and dried The collodion is burnt off the first time the mantle is placed in position, and it is no longer to be carried about The incandescent or light-emitting power of the mantle is somewhat sensitive to variations in the composition of the mixture of earths With the above-named mixture, the light has ten times the illuminating power of a flat flame burner using the same amount of gas

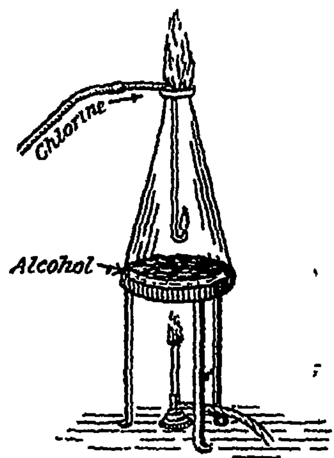


FIG 291

If the proportion of thoria to ceria in the ash of the mantle differs very much from 99 to 98 per cent of thoria and 1 to 2 per cent of ceria, the luminosity of the mantle is reduced If a greater proportion of ceria be present, the diminished luminosity is said to be due to the fact that the mantle cannot all be raised by the flame to full incandescence Thoria alone gives very little light If a minute quantity of ceria be distributed over the poor heat conducting thoria, the mass of ceria is so small that it can be readily heated to the high temperature needed for producing an intense incandescence The luminosity of the mantle increases with about the fifth power of the temperature

Davy's solid particle theory—As a result of his classical investigations on flame, Humphry Davy (1815) was led to suggest that "the superior light from a stream of coal gas might be owing to a decomposition of a part of the gas towards the interior of the flame where the air is in smallest quantity, and the deposition of solid carbon, which first by its ignition and afterwards by its combustion, increased in a high degree the intensity of the light" And finally, Davy concluded that "whenever a flame is remarkably brilliant or dense (*opaque*) it may always be concluded that some solid matter is produced in it, on the contrary, when a flame is extremely feeble and transparent, it may be inferred that no solid matter is formed" We have seen how carbon can be produced in a hydrocarbon flame Davy's generalization is not always satisfactory because

burning phosphorus, hydrogen phosphide, carbon disulphide in oxygen or in nitric oxide, hydrogen arsenide, etc, give luminous flames although the temperature of the flame is too high to allow the presence of solid products of combustion This is confirmed by the fact that these flames give no shadows by Soret's optical test Consequently, however true the solid particle theory may be for some hydrocarbon flames, it does not describe all the story

Frankland's dense hydrocarbon theory—H. Davy showed that the luminosity of flames is increased by pressure and diminished by rarefaction E Frankland (1867) found a direct relation between the luminosity of flames and the pressure Using the flame of hydrogen burning under a pressure of 12 atmospheres, a reduction of the pressure to 3 atmospheres, diminished the luminosity 99 per cent. as illustrated in Fig 292 Arguing from the fact that luminous flames are known which contain no solids, that dense gases and vapours give flames more luminous than gases of low density, and that feebly luminous flames become luminous when the surrounding atmosphere is compressed, Frankland inferred that the luminosity of ordinary flames such as coal gas is due to the glow of dense hydrocarbons rather than to the presence of solid particles, Lewes considers that the "dense hydrocarbon" in the flame of coal gas and related gases is acetylene, hence, the so called **acetylene theory of luminosity** In the particular case of hydrocarbon flames, as interpreted in the preceding section, it does not appear that this hypothesis is a complete explanation When the pressure of the atmosphere is altered, the dense hydrocarbons themselves give opaque flames containing solid matter The phenomenon is complicated by changes in the conditions of equilibrium of the products of combustion, and it is probable that the decomposition of the hydrocarbons in the "innermost parts of the flame" is facilitated by increasing the pressure

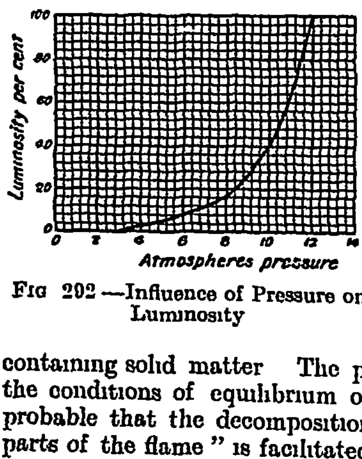


FIG 292—Influence of Pressure on Luminosity

However, it is highly probable that dense vapours, as well as incandescent solids, do produce luminosity Two distinct effects can be observed in burning hydrogen phosphide a greenish glow due to the oxidation of the phosphorus which shows best when the phosphide is largely diluted with carbon dioxide, and a yellowish white light best seen when phosphorus burns in air or oxygen This is no doubt due to the glowing of phosphorus pentoxide which, although in the state of *vapour*, can be made to emit a yellowish white glow when the temperature has attained a certain point Similar results can be obtained with silicon hydride, but in this case the glow is due to *solid* silica

Influence of temperature on luminosity—Just as a variation of pressure modifies the luminosity of burning gases, so does a variation of temperature, as indicated on pp 751–2 The temperature attained by the combustion of gases in oxygen is greater than in air, owing to the absence of diluting nitrogen In consequence, combustibles burn far more brilliantly in oxygen than in air The flame of carbon disulphide in air is

nothing like so brilliant as in oxygen, the flame of hydrogen phosphide in air is brilliant, but in oxygen the flame is of dazzling brilliance Phosphorus burns in chlorine with a far more luminous flame when the chlorine is hot than when cold Carbon monoxide in oxygen burns with a flame appreciably luminous Similarly with flames known to contain solid matter Magnesium and silicon hydride burn far more brightly in oxygen than in air The effect of increasing the temperature of the gases in a non-luminous Bunsen's burner has been previously discussed

To summarize A general explanation of luminosity to cover all cases is wanting To say that "luminosity is caused by the intense vibratory motions of the molecules induced by the act of chemical union" is not very satisfactory, because it tells us little more than that "flames are luminous because they emit a bright light," until it is shown why the "intense vibratory motions of the molecules" of many non-luminous flames do not give light In special cases, the luminosity of flames can be traced to the "glowing" produced either by the products of combustion (*e g* hydrogen phosphides, silicon hydride) or intermediate products of combustion (*e g* hydrocarbon flames) The glowing may be due to the presence of glowing vapours (*e g* hydrogen phosphide) or to glowing solid matter (*e g* silicon hydride) The luminosity of flames is in general increased by raising the temperature or increasing the pressure.

§ 12 The Bunsen's Burner

1 **Structure of the burner** —The gas burner devised by Robert Bunsen about 1855, will be very familiar to chemistry students Its construction is easily understood Unscrew the burner tube from the base The burner consists of three parts (1) The base *A*, Fig 293, supplied with gas by means of a rubber tube connected with the main The gas escapes from a small opening in the base, which may or may not have a screw "pin hole" nipple By lighting the gas issuing from the base, a long thin pencil of flame is obtained. (2) The burner tube, *B* has a couple of openings near the base, and these can be closed, partially closed, or opened by turning the air regulator (3) The air regulator, *C*, is a short cylindrical tube fitted with holes to correspond with the holes in the burner tube There are numerous modifications, that just described may be taken as typical Some are provided with an attachment for forcing in air under pressure, forming the so-called *blast burners* Replace the air regulator and burner tube

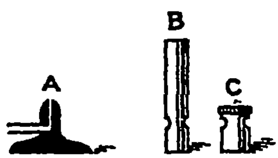


FIG 293 —Parts of Bunsen's Burner

2 **How the burner does its work** —If the air-holes are closed, an ordinary luminous gas flame is obtained If the air-holes are opened, the jet of gas from the small orifice produces a partial vacuum in the neighbourhood of the jet, and, in consequence, air is drawn into the air-holes, and mixes with the gas in the burner tube The reduction in pressure is conveniently shown by closing one of the air-holes with a piece of gummed paper, and affixing a small manometer, Fig 294, to the other air-hole by means of a perforated cork [1] When the manometer is charged with a

[1] Or solder a piece of brass tubing to the burner

liquid—coloured to enable it to be seen better—and the gas is turned on, the movement of the liquid towards the burner shows that the air holes exert a slight suction When the gas is turned off, the liquid in the manometer returns to its former position

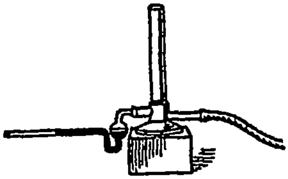


Fig 294 —Pressure at Air holes of Bunsen's Burner

A certain ratio must exist between the proportion of air and gas in the burner tube in order to get the gas to burn quietly with a blue flame—the so called Bunsen's flame This is observed by placing the regulator in several different positions and gradually turning off the gas When the air holes are fully open, and the gas is gradually turned off, a point is reached when the flame begins to flicker, and finally " strikes back " afterwards burning at the bottom of the tube As a matter of fact, the mixture of air and gas burning in the Bunsen's burner is explosive when the gas is burning quietly, the rate at which the flame travels in the explosive mixture of air and gas is less than the rate at which gas is issuing from the burner, when more air or less gas is introduced, the speed at which the explosive flame can travel is increased, when the rate of the explosive flame and the speed of the gas issuing from the burner are nearly equal the flame reaches the unstable condition, any further increase in the amount of air or decrease in the amount of gas gives an explosive mixture in which the explosive flame can travel faster than the issuing gas, the flame then " strikes back " This phenomenon is best studied by clamping a long tube—5 or 6 feet long, and about 1¼ inches wide—vertically over a Bunsen's burner, Fig 295 Plug the space between the Bunsen's burner and the glass tube with cotton wool Close the air holes of the former, and light the gas (Fig 295) Gradually remove the cotton wool until a large blue Bunsen's flame is obtained Then open the air-holes of the Bunsen's burner gradually, and a point will be reached when the flame " strikes back " with a loud though harmless report.

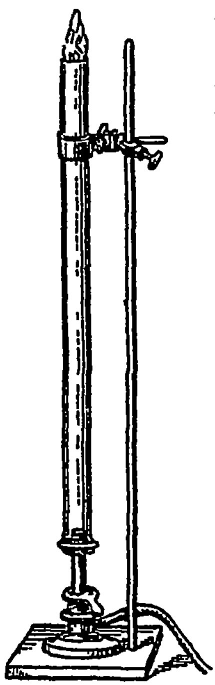


Fig 295 —Striking back of Bunsen's Flame

In the Bunsen's burner, the proportion of air to gas is between 2 and 3 volumes of air per one volume of gas, but for complete combustion of the gas, about 6 volumes of air are needed If such a mixture were sent through an ordinary Bunsen's burner, the flame would " strike back "—for the reasons indicated above G Méker, however, has designed a burner in which such a mixture can be burnt—Méker's burner From the sectional diagram, Fig 296, it will be seen that the air holes are larger than usual, and a deep grid hinders the flame " striking back." Since the gas issuing from the burner has enough air for complete combustion, the flame is practically a " solid cone " of burning gas, and there is no " inner cone of unburnt gas " In consequence, the temperature of the interior of the flame is rather greater than the temperature near the outside

3 Why is the flame non-luminous?—(a) Oxidation. It was formerly taught that the non luminosity of the Bunsen's flame was exclusively due to the influence of the admixed oxygen bringing about rapid and complete combustion so that instead of the hydrocarbons decomposing in a series of intermediate stages, they were burnt more directly to carbon dioxide and water Experiments by V B Lewes on the amount of different gases required to produce the non-luminous flame showed that one volume of coal gas required for the non-luminous flame

Mixture of O N	1 0	1 1	1 2	1 3	1 5 (air)
Volume required	0 5	1 0	1 5	2 0	2 3 vols

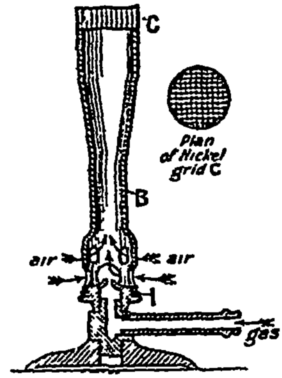


FIG 296 —Méker's Burner

This shows that oxygen intimately mixed with the coal gas exerts an oxidizing effect and facilitates rapid combustion (b) The cooling of the flame by different gases This, however, is not all the story Inert gases like nitrogen, carbon dioxide, and steam produce non-luminous flames Thus,

Gas	Air	Nitrogen	Carbon monoxide	Carbon dioxide
Volumes required	2 3	2 3	5 1	1 3

These facts coupled with the known effect of temperature on the luminosity of flames, show that the air reduces the luminosity of the Bunsen's flame by chilling the reacting gases (c) The raising of the temperature of the decomposition of coal gas by admixture with inert gases Lewes has shown, other things being equal, that coal gas, when mixed with nitrogen, is probably more stable when heated in the inner cone than when nitrogen is absent, and further, a different set of decomposition products are obtained when the hydrocarbons are burned at the higher temperature Further details on the nature of the Bunsen's flame are indicated in preceding sections

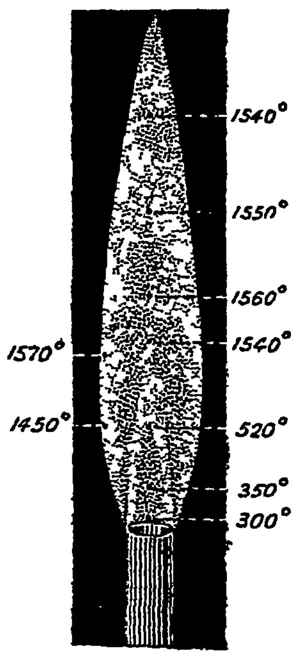


FIG 297 —Temperatures of Different Parts of the Bunsen's Flame (Féry)

4 Oxidizing and reducing flames —The outer mantle of the flame, where there is an excess of oxygen, is oxidizing, and the inner region, where combustion is not complete, is reducing This can be confirmed by holding a piece of copper wire across different parts of the flame Advantage is taken of this in qualitative analysis where "flame reactions" furnish valuable indications of the composition of a mixture

5 The temperature of the Bunsen's flame —The temperature of different parts of the Bunsen's flame, as recorded by a thermocouple inserted in different parts of the flame (C Féry) is shown in Fig 297 The published determinations of the maximum temperature of the Bunsen's flame are somewhat discordant The discrepancy arises from the

presence of several errors in the method used for the determination The most satisfactory methods show that the maximum temperature is somewhere between 1800° and 1870° Valuable information respecting the composition of certain mixtures can be obtained by taking advantage of the different volatility of salts, and the different temperatures of the Bunsen's flame For instance, potassium salts can be volatilized so as to give the flame reaction for potassium, before the sodium has begun to volatilize, if the mixture of the two salts be held in the cooler part of the Bunsen's flame near the burner

The temperature obtainable by heating a small body in a Bunsen's flame is said to range from 1100° to 1350°, in a Méker's flame, from 1450° to 1500°, in a petrol blow-pipe flame, from 1500° to 1600°, in the oxy hydrogen flame, about 2000°, in the oxy acetylene flame, about 2400°, and in the electric arc, about 3500°

According to Féry (1904), the flame temperature of a Bunsen's flame, fully aerated, is 1871°, and according to V B Lewes (1895), the maximum

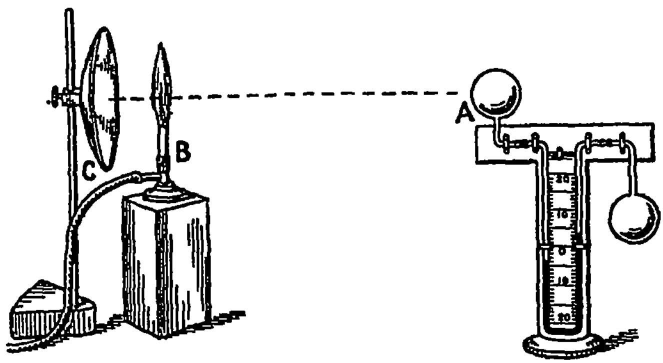


FIG 298 —Radiation of Heat by Luminous and Non luminous Flames

temperature of a luminous flame is 1330° Hence, it might be concluded that the Bunsen's flame develops more heat than the luminous flame burning the same amount of gas. This conclusion would be erroneous. Given just sufficient air for complete combustion both flames develop the same amount of heat (Hess' law) The reason the temperature of the luminous flame is less than that of the non luminous flame is due to the fact that a greater quantity of the heat generated by the combustion of the gas in the luminous burner is lost by radiation When the luminous flame is placed under a vessel less heat strikes the vessel, because more heat is radiated into space According to J Tyndall, the Bunsen's flame radiates 12 per cent of its heat into space, while the luminous flame radiates 30 per cent The difference in the heat radiating power of the two flames can be illustrated by the following experiment A differential thermometer, *A*, Fig 298, is arranged so that the heat from a Bunsen's flame, *B*, is concentrated on one of the bulbs by means of a reflector, *C* A rise of the temperature of the bulb is shown when the air holes of the Bunsen's burner are closed and the gas burns with a luminous flame The difference between the two flames thus depends on the way the heat is distributed. If all the heat in both flames be utilized, the one gives out as much heat

as the other The heat of the Bunsen's flame is more local and concentrated than the heat of the same gas burning with a luminous flame The Bunsen's flame is therefore best for boiling, etc, where the heat must be concentrated on the bottom of a vessel or as locally as possible The Bunsen's flame, moreover, is not liable to deposit soot on the bottom of the vessel being heated and so obstruct the conduction of heat from the flame to the vessel In certain industrial operations the luminous flame often gives better results than the non-luminous flame for heating large enclosures directly by flame The non-luminous flame heats more where it touches, the luminous flame radiates heat to its surroundings, and this helps to keep the temperature of large enclosures uniform

Questions

1 Assuming exterior conditions to be the same, which will probably show the greater explosive effect, a mixture of 500 c c of oxygen and 500 c c of hydrogen, or a mixture of 300 c c of oxygen and 600 c c of hydrogen, and why ?—*American Coll*

2 Describe lecture experiments that illustrate—(*a*) that hydrogen burns with a luminous flame when benzene is added to it, (*b*) that a flame "strikes back" through a tube when a sufficient amount of air is mixed with coal gas, (*c*) that the interior of the inner cone of a round flame is cool, (*d*) that oxygen will burn in coal gas —*Cornell Univ, U S A*

3 Give three reasons for the non luminosity of the flame from a Bunsen's burner When will such a flame "strike back" ? What causes the luminosity of the ordinary gas flame ? Why does the amount of carbon dioxide in the atmosphere remain practically the same ?—*Cornell Univ, U S A*

4 Describe and explain as fully as you can all the chemical changes which occur in the burning of a deep anthracite coal fire Explain any differences between such a fire and one of bituminous coal —*American Coll*

5 State some of the consequences which would conceivably follow if the percentage of oxygen in the atmosphere were to increase to double the present proportion. Explain your answer, and cite experiments in support of your statements —*American Coll*

6 What influence had the phlogistic theory on the progress of chemistry ? Why was the anti phlogistic theory incomplete before the composition of water was known ?—*Science and Art Dept*

7 What is a reducing agent ? Name three agents capable of effecting the reduction of ferric chloride in aqueous solution, and explain the chemical changes involved By what test could the completion of the reduction be ascertained ?—*Sheffeld Univ*

8 Write a brief history of the theory of phlogiston with an account of the discoveries which finally led to its rejection —*Science and Art Dept*

9 What would be the effect of heating lead chloride to redness, (*a*) in a current of hydrogen, (*b*) with potassium carbonate, (*c*) with charcoal ?—*Owens Coll*

10 Define the terms reducing and oxidizing agents and give three examples of each Define combustion in (*a*) the popular and (*b*) the strictly scientific sense Will air burn ?—*Princeton Univ, U S A*

11 Discuss the theories that have been proposed to account for luminous combustion Describe the flames of the following substances and their products of combustion, viz carbon monoxide marsh gas, olefiant gas, phosphine, ammonia, hydrogen sulphide, and silicon hydride —*London Univ.*

12 Describe the sources, preparation, and properties of the earths used in the manufacture of mantles for incandescent lighting In what proportion are these earths used, and what is the part played by each in producing the intense light emitted by the incandescent surface ?—*Board of Educ*

CHAPTER XXXIX

THE COMPOUNDS CONTAINING CARBON AND NITROGEN

§ 1 Ferrocyanides and Ferricyanides

Potassium ferrocynaide, K_4FeCy_6—When nitrogenous refuse (blood, horns, leather scraps, etc) is charred, and the black mass is ignited with potash and iron filings, something is formed which passes into solution when the mass is lixiviated with water The aqueous solution on evaporation gives yellow crystals of potassium ferrocyanide with the empirical composition, $K_4FeC_6N_6\ 3H_2O$ It is convenient to represent the univalent group "CN" by the symbol "Cy," and accordingly the formula is written $K_4FeCy_6\ 3H_2O$ The same salt is obtained from the "spent oxide" of the "purifiers" of gas works which are used (*q v*) to remove the sulphur and cyanogen compounds from the gases formed during the distillation of coal The "spent oxide" is boiled with lime The soluble calcium ferrocyanide is leached from the mass, and converted into potassium salt by the treatment with potassium carbonate The resulting potassium ferrocyanide is purified by crystallization Sometimes the cyanogen compounds are removed from the coal gas before it reaches the purifiers by washing the gas in an alkaline solution with ferrous carbonate in suspension

Properties of potassium ferrocyanide—Potassium ferrocyanide crystallizes in laminated, sulphur yellow crystals with three molecules of "water of crystallization," $K_4FeCy_6\ 3H_2O$ The salt is soluble in water, the solution has a bitter taste, but is not particularly poisonous The salt loses its "water of crystallization" on warming, and the anhydrous salt remains behind as a white powder The salt is decomposed when heated, forming potassium cyanide, KCy, and an impure iron carbide $K_4FeCy_6 \rightarrow 4KCy + FeC_2 + N_2$ When warmed with *dilute* sulphuric acid, hydrogen cyanide (*q v*) is formed, with *concentrated* sulphuric acid, carbon monoxide is evolved

$$K_4FeCy_6 + 6H_2O + 6H_2SO_4 = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

Potassium ferrocyanide decomposes when ignited out of contact with the air and forms a complex mixture of potassium cyanide, iron carbide, etc

Ferrocyanic acid, H_4FeCy_6—When a saturated solution of potassium ferrocyanide, freed from dissolved air by boiling, is treated with concentrated hydrochloric acid in the cold, a white crystalline powder called ferrocyanic acid is formed, it has the empirical formula, H_4FeCy_6 Ferrocyanic acid turns blue on exposure to the air owing to the partial decomposition of the salt and the formation of Prussian blue (*q v*)

Sodium nitroprusside, $Na_2FeNOCy_5.2H_2O$.—When, say, four grams of powdered potassium ferrocyanide are boiled for half an hour with 4 c.c. of concentrated nitric acid diluted with its own volume of water, and the cold solution made alkaline with sodium hydroxide, ruby-red crystals of sodium nitroprusside are obtained. Here the radicle NO takes the place of one Na atom, and one Cy radicle, in sodium ferrocyanide. The salt is sometimes called *sodium nitroferrocyanide*. A solution of sodium nitroprusside is sometimes used as a test for sulphides since it gives a deep violet coloration with soluble sulphides.

Potassium ferricyanide, K_3FeCy_6.—If an aqueous solution of potassium ferrocyanide be treated with oxidizing agents like chlorine, bromine, nitric acid, hydrogen peroxide, etc., it acquires a dark reddish colour, and crystals of potassium ferricyanide separate when the solution is concentrated by evaporation: $2K_4FeCy_6 + Cl_2 = 2KCl + 2K_3FeCy_6$. The potassium ferricyanide is separated from potassium chloride by re-crystallization. The solution is a mild oxidizing agent in alkaline solutions, for it oxidizes "reducing agents" like sodium thiosulphate, hydrogen sulphide, etc., re-forming potassium ferrocyanide: $4K_3FeCy_6 + 4KOH = 2H_2O + 4K_4FeCy_6 + O_2$. When a saturated solution of potassium ferricyanide is treated with concentrated hydrochloric acid, in the cold, reddish-brown crystals of ferricyanic acid, H_3FeCy_6, separated from the solution.

Various salts of ferrocyanic and ferricyanic acids have characteristic colours, and consequently, potassium ferrocyanide and ferricyanide—particularly the former—are used in qualitative analysis.

TABLE LVI.—PROPERTIES OF FERRO- AND FERRI-CYANIDES.

	Ferrocyanides added to	Ferricyanides added to
Ferric chloride	Deep blue, precipitate of Prussian blue, insoluble in hydrochloric acid, soluble in oxalic acid	No precipitate in neutral solutions, but the solution is coloured green or blue.
Ferrous chloride	Bluish white precipitate which rapidly darkens on exposure to air, or by adding a drop of bromine	Deep blue precipitate of Turnbull's blue
Copper sulphate	Reddish brown precipitate	Yellowish-green precipitate
Zinc sulphate	White precipitate	Orange precipitate
Silver nitrate	White precipitate	Reddish brown precipitate

Ferric ferrocyanide, $Fe_4(FeCy_6)_3$.—This compound is also called Prussian blue. It is formed, as indicated in the preceding table, when a solution of potassium ferrocyanide is added to a solution of a ferric salt. It is insoluble in hydrochloric acid, but soluble in oxalic acid, forming a deep blue solution. When heated with concentrated sulphuric acid Prussian blue yields hydrocyanic acid; and when boiled with alkaline hydroxides, ferric hydroxide is precipitated, and alkaline ferrocyanide remains in solution. Besides the "insoluble" Prussian blue, a "soluble" or colloidal Prussian blue is formed when a ferric salt is added to a solution of potassium ferrocyanide, or a ferrous salt to a solution of potassium ferricyanide. By the addition of salt to the solution, the "soluble"

Prussian blue is coagulated or "salted out," and the precipitate is then "insoluble" Prussian blue

Ferrous ferricyanide, $Fe_3(FeCy_6)_2$—When potassium ferricyanide is added to neutral or acid solutions of ferrous chloride, a dark blue precipitate of ferrous ferricyanide, also called "Turnbull's blue," is formed If potassium ferrocyanide is added to a ferrous salt, ferrous potassium ferrocyanide, FeK_2FeCy_6, or ferrous ferrocyanide, Fe_2FeCy_6 is formed

§ 2 Hydrocyanic Acid and the Cyanides

Potassium cyanide, KCy —Potassium cyanide was formerly made by heating potassium ferrocyanide either alone or mixed with potassium carbonate in an iron crucible to a red heat $K_4FeCy_6 + K_2CO_3 = 5KCy + KCyO + Fe + CO_2$ The mass was lixiviated with water, and the solution evaporated to dryness, fused, and cast into sticks The commercial salt always contains some potassium cyanate, KCyO Potassium cyanide is extensively used in electroplating, gilding, the extraction of gold from quartz, and in photography Fused potassium cyanide is a powerful reducing agent, and it liberates metals from their oxides, and is at the same time converted into potassium cyanate (*q v*) $SnO_2 + 2KCy = 2KCyO + Sn$ Hence potassium cyanide is used in metallurgy and in analytical work When heated alone, potassium cyanide fuses without decomposition in the absence of air, but if air be present, it is partially converted into potassium cyanate (*q v*) Potassium cyanide is soluble in water and in hot alcohol The aqueous solution is very unstable, p 327, and when boiled with water, it slowly decomposes, forming ammonia and potassium formate, H CO OK.

Manufacture of cyanides —Cyanides can be manufactured cheaply in several ways By fusing potassium ferrocyanide with sodium all the cyanogen, Cy, is converted into cyanide $K_4FeCy_6 + 2Na = 2NaCy + 4KCy + Fe$ The iron can be separated from the fused mass, and a mixture of sodium and potassium cyanides remains The mixture can be used for the extraction of gold, etc If ammonia be passed over heated sodium, sodamide is formed $2NH_3 + 2Na = 2NH_2Na + H_2$, as indicated on p 538, and if the fused mass be run over red hot carbon sodium cyanide is formed $2NaNH_2 + 2C = 2H_2 + 2NaCy$

A Frank and N Caro patented a process in 1895 for the fixation of the nitrogen of atmospheric air by heating calcium or barium carbides in an atmosphere of nitrogen between 1000° and 1100° Nitrogen, it will be remembered, is a by-product in Linde's process for separating oxygen from liquid air The absorption of nitrogen by the carbides commences about 700°, but the reaction is incomplete, at 1100°, however, the absorption is practically complete, and calcium cyanamide, $CaCN_2$, that is, Ca=N—Cy, is formed $CaC_2 + N_2 \rightarrow CaCN_2 + C$ A large amount of heat is evolved at the same time The mixture of carbon and calcium cyanamide so obtained is known in commerce as "nitrolime" or "kalkstickstoff" When in contact with water, calcium cyanamide forms dicyandiamide $(CyNH_2)_2$, thus $2CaCN_2 + 4H_2O = 2Ca(OH)_2 + (CyNH_2)_2$, and when treated with superheated steam, calcium cyanamide forms calcium carbonate and ammonia $CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$ Calcium cyanamide is used as a fertilizer, and in the manufacture of cyanides, for

if calcium cyanamide be melted with a suitable flux—sodium chloride or carbonate—sodium cyanide is produced $CaCN_2 + C = CaCy_2$, and $CaCy_2 + Na_2CO_3 = CaCO_3 + 2NaCy$

Complex cyanides —When simple and complex cyanides are boiled with water holding yellow mercuric oxide in suspension, mercuric cyanide, $HgCy_2$ is formed, thus, with potassium ferrocyanide $K_4FeCy_6 + 3HgO + 3H_2O = Fe(OH)_2 + 4KOH + 3HgCy_2$ The decomposition of the cyanides by mercuric oxide is utilized in quantitative analysis for the separation of cyanides Silver cyanide is formed as a white insoluble powder when potassium cyanide is added to a soluble silver salt The precipitate is soluble in excess, forming a complex potassium argento-cyanide, $KAgCy_2$ If nitric acid be added to the solution, silver cyanide is precipitated. This complex cyanide is used in electroplating, p 303 This reaction is used for the *volumetric determination of potassium cyanide* A standard solution of silver nitrate is added to the cyanide solution until a precipitate is just formed. The burette is then read, and the amount of potassium cyanide corresponding with the silver solution dropped from the burette is computed from the equation $2KCy + AgNO_3 = KAgCy_2 + KNO_3$ Each atom of silver corresponds with two molecules of potassium cyanide Any further addition of the silver nitrate will decompose some of the potassium cyanide and form a precipitate

Cuprous cyanide also dissolves in potassium cyanide forming a similar complex salt $CuCy + 3KCy \rightleftharpoons K_3CuCy_4$ The potassium cuprocyanide so obtained is sufficiently stable to be unaffected by hydrogen sulphide in neutral or alkaline solution, the cadmium complex cyanide, K_2CdCy_4, is decomposed under the same conditions A common method of separating copper from cadmium depends upon this fact

The cyanides are remarkable in forming a series of complex cyano-salts remarkable for their stability Potassium ferro- and ferri-cyanides, and potassium silver cyanide have been previously studied. If the method worked out for the graphic formula of ammonium chloride were applied consistently it might be inferred the iron in the ferrocyanides is 10-valent, and 9-valent in the ferricyanides. Very little is known about the relative position of the atoms in these molecules The complex cyanides are conveniently formulated according to Werner's scheme (R univalent), p 647, in illustration

$[AgCy_2]R$	$[AuCy_2]R$	$[ZnCy_2]R$	$[Cu_2Cy_3]R$
$[ZnCy_4]R_2$	$[PtCy_4]R_2$	$[CuCy_3]R_2$	$[NiCy_4]R_2$
$[FeCy_6]R_3$	$[CoCy_6]R_3$	$[MnCy_6]R_3$	$[CrCy_6]R_3$
$[FeCy_6]R_4$	$[CoCy_6]R_4$	$[MnCy_6]R_4$	$[CrCy_6]R_4$

In sodium nitroprusside, or sodium nitroferricyanide, we have $[Fe(NO)Cy_5]Na_2$. The union of ferrous and potassium cyanide in the case of potassium ferrocyanide, and of ferric and potassium cyanide in the case of potassium ferricyanide, must involve a profound change in the molecules concerned. The iron ceases to act as a basic element, but becomes an integral part of the acidic radicle Potassium ferricyanide is not therefore a double salt, $FeCy_3 \cdot 3KCy$, and potassium ferrocyanide is not a double salt, $FeCy_2 \cdot 4KCy$ since the iron cannot be separated by precipitation as is the case with the iron in ordinary ferrous and ferric salts, and aqueous solutions of potassium ferrocyanide, according to the ionic hypothesis contain the quadrivalent ion, $FeCy''''$, and the

ferricyanides, the tervalent ion $FeCy_6'''$, because the iron appears at the anode not the cathode during electrolysis

Hydrogen cyanide, HCN—Hydrogen cyanide is made by distilling a mixture of powdered potassium cyanide with a mixture of equal volumes of sulphuric acid and water, if concentrated acid be used, a considerable amount of carbon monoxide is evolved. The vapour is passed through a U-tube containing calcium chloride to remove the water The dry hydrogen cyanide is led through a U tube surrounded by ice, and the gas condenses to a colourless liquid The gas is also made by passing dry hydrogen sulphide over dry mercury cyanide and condensing the vapour to a liquid as before Pure hydrogen cyanide is one of the most deadly poisons known, and hence great care must be taken in experiments with hydrogen cyanide and indeed with cyanides generally The liquid boils at 26 5°, and freezes at −15° to a white solid It dissolves in water in all proportions, and the solution—called **hydrocyanic acid**—has the smell of bitter almonds K. W Scheele discovered hydrocyanic acid in 1782, J L Gay Lussac made the anhydrous compound, HCN, and established its composition in 1811 A 10 per cent aqueous solution is often called "prussic acid," and a 2½ per cent solution is used in medicine The ordinary aqueous acid can be made by the distillation of, say, 0 5 gram of potassium ferrocyanide with 100 c c of 10 per cent. sulphuric acid until 10 c c of a dilute aqueous solution of the acid has collected in the receiver The latter process is also used on a large scale

Hydrocyanic acid is monobasic and the salts, as indicated above, are called cyanides Hydrocyanic acid is one of the weakest of acids, and this corresponds with its low electrical conductivity Some ammonium cyanide is formed when ammonia is passed over red hot charcoal and when a series of electric sparks are passed through a mixture of acetylene and nitrogen When chlorine gas is passed into hydrocyanic acid, a colourless liquid called "liquid" **cyanogen chloride** with the empirical formula, CyCl, is produced $HCy + Cl_2 = HCl + CyCl$ This polymerizes on standing and forms "solid" cyanogen chloride, or **cyanuric chloride**, Cy_3Cl_3 The action of bromine on a metallic cyanide or on hydrocyanic acid furnishes **cyanogen bromide, CyBr** This substance sublimes at from 60°–65°, forming transparent crystals When treated with a well-cooled aqueous solution of sodium trinitride, NaN_3, p 552, freshly prepared cyanogen bromide gradually dissolves If the solution be extracted with ether, and the ethereal solution be evaporated in a current of dry air, a colourless liquid is obtained which soon crystallizes The crystals have the empirical composition CN_4, and they appear to be **cyanogen trinitride** or **cyanogen hydrazoate**, $N_3—C{\equiv}N$, formed by the reaction $N_3Na + CyBr = NaBr + N_3Cy$ The compound is explosive decomposes at 70°, melts between 35 5° and 36°, dissolves in water, and the aqueous solution gradually hydrolyzes $CyN_3 + 2H_2O = N_3H + CO_2 + NH_3$ The compound gradually polymerizes on keeping

When hydrocyanic acid is heated with mineral acids, or when potassium cyanide is boiled with water, formic acid or rather ammonium formate is produced $HCy + 2H_2O = H.CO\,OH + NH_3$ When ammonium formate is distilled with some dehydrating agent—say, phosphorus pentoxide—the formic acid is resolved into hydrogen cyanide $H\,COONH_4 = HCy + 2H_2O$ These facts, together with much evidence discussed

in text-books of organic chemistry, show that the hydrogen atom in hydrogen cyanide is probably united directly with the carbon atom and not with the nitrogen atom, and that the formula of hydrogen cyanide is H—C≡N The fact that the hydrogen of hydrocyanic acid can be displaced by the metals corresponds with the close analogy between hydrocyanic and hydrochloric acids There are some reasons for supposing that there are two series of compounds derived from an acid with the empirical formula, HCN, the one set called the cyanides or nitriles corresponds with H—C≡N, and the other, called isocyanides or isonitriles, with H—N≡C These compounds are discussed in organic chemistry

§ 3 Cyanogen

Cyanogen, Cy_2, is a gas made by heating mercuric or silver cyanide in a hard glass tube $HgCy_2 = Hg + Cy_2$ The gas is best collected over mercury, Fig 44 The yield of cyanogen is much less than the theoretical owing to the simultaneous formation of a peculiar dark brown powder called paracyanogen This substance appears to be a polymer of cyanogen, because if continuously heated it furnishes ordinary cyanogen On heating a mixed solution of potassium cyanide and copper sulphate, a yellow precipitate of cupric cyanide, $CuCy_2$, is first formed, and this is immediately decomposed into cuprous cyanide, CuCy, and cyanogen $4KCy + 2CuSO_4 = 2K_2SO_4 + 2CuCy + Cy_2$ Small quantities of cyanogen occur in blast furnace gases.

Cyanogen is a colourless poisonous gas with a faint odour which reminds some people of the smell of peaches Cyanogen burns with a violet coloured flame forming carbon dioxide and nitrogen It condenses to a liquid under a pressure of four atmospheres at ordinary temperatures, and at ordinary pressures it furnishes a liquid boiling at 20 7°. The liquid freezes to a white solid melting at −34° The gas has a vapour density of 52 ($H_2 = 2$), which corresponds with the molecule C_2N_2 Cyanogen dissolves readily in water The aqueous solution deposits a peculiar brown flocculent mass—azulmic acid—on standing, ammonium oxalate, hydrogen cyanide, and carbon dioxide are formed at the same time Cyanogen unites directly with the alkali metals forming cyanides. The name cyanogen is derived from *κύανος* (cyanos), dark blue, and *γεννάω* (gennao), I produce Cyanogen was isolated by J L Gay-Lussac in 1815

Cyanogen bears some analogy with chlorine For instance, when it is passed into a solution of potassium hydroxide, it forms potassium cyanate, KOCy, and potassium cyanide, KCy, just as chlorine under similar conditions forms potassium hypochlorite KOCl, and potassium chloride, KCl The silver salts, etc, also have many analogous properties.

§ 4 Cyanic Acid and the Cyanates

Potassium cyanate, KO—CN —This salt is produced when potassium cyanide is slowly oxidized in air, and it is usually made by heating potassium cyanide or ferrocyanide with an oxidizing agent—litharge, red lead, potassium permanganate, etc $KCy + PbO = Pb + KOCy$ The potassium cyanate is extracted by lixiviating the mass with dilute

alcohol, and concentrating the alcoholic solution by evaporation Potassium cyanate is a colourless crystalline powder readily soluble in water and in dilute alcohol The aqueous solution readily decomposes $KOCy + 2H_2O = NH_3 + KHCO_3$ The corresponding acid, HOCy, decomposes so rapidly into carbon dioxide and ammonia $HOCy + H_2O = CO_2 + NH_3$, that cyanic acid cannot be prepared by the decomposition of its salts with mineral acids

Cyanic acid, HOCy —If cyanuric chloride, Cy_3Cl_3, be treated with water, cyanuric acid, $H_3Cy_3O_3$, is formed $Cy_3Cl_3 + 3H_2O = 3HCl + H_3Cy_3O_3$, as a crystalline tribasic acid If cyanuric acid be heated in a tube, and the vapours passed through a U-tube cooled by immersion in a freezing mixture, an unstable liquid with the empirical formula HCyO is obtained $H_3Cy_3O_3 = 3HCyO$ If the temperature be raised above 0°, cyanic acid rapidly polymerizes into a hard, white, opaque mass called cyamelide

Ammonium cyanate, NH_4CyO —This salt is formed as a white crystalline powder when dry ethereal solutions of ammonia and cyanic acid are mixed together It is also formed when a mixture of carbon monoxide and ammonia is passed over heated platinized asbestos, or subjected to the silent or spark electric discharge On evaporating an aqueous solution of ammonium cyanate, F Wöhler, in 1828, synthesized urea, $CO(NH_2)_2$ (p 685), isomeric with ammonium cyanate With potassium hydroxide, ammonium cyanate forms potassium cyanate

§ 5 Thiocyanic Acid and the Thiocyanates

If the alkaline cyanides be fused with sulphur, a change, analogous with the oxidation of the alkaline cyanide, occurs, and the so called thiocyanates, or "sulpho cyanides," are formed $KCy + S = KCyS$ The fused mass, when cold, is lixiviated with dilute alcohol, and the alcoholic solution, when concentrated by evaporation, furnishes colourless deliquescent crystals of potassium thiocyanate, KCNS Ammonium thiocyanate is conveniently made by digesting concentrated ammonia with carbon disulphide $4NH_3 + CS_2 = NH_4SCy + (NH_4)_2S$ The thiocyanates give a blood red ferric thiocyanate with ferric salts, and no coloration occurs with the ferrous salts if ferric salts be absent According to the ionic hypothesis, the red colour is supposed to be due to the un ionized molecules, $Fe(CyS)_3$, since neither the ferric ion Fe nor the thiocyanate ion CyS′ are coloured The red coloration is intensified if more ferric salt, or more thiocyanate be added to the solution, because the "addition of a common ion" causes part of the ionized salt to recombine to form molecules of the coloured ferric thiocyanate When silver nitrate is added to a solution of potassium thiocyanate, a white flocculent precipitate of silver thiocyanate, AgCyS, separates This is insoluble in dilute mineral acids This reaction is the basis of Volhard's volumetric process for the determination of silver Mercuric thiocyanate, $Hg(CyS)_2$, made by adding mercuric chloride to a solution of potassium thiocyanate, is an insoluble powder which when washed and dried takes fire on ignition and forms a voluminous ash Pellets made from the dry powder, when ignited, form long snake-like tubes—the so called "Pharaoh's serpents." Thiocyanates are used

for dyeing A certain amount of ammonium thiocyanate is found in the "gas liquor" and in the "spent oxide" of the gas works

Thiocyanic acid, HCyS—This acid is made by distilling potassium thiocyanate with dilute sulphuric acid under reduced pressure, and passing the vapour through a tube containing calcium chloride to remove the vapour of water, and then through a U-tube cooled by a freezing mixture The volatile liquid is quickly polymerized if removed from the freezing mixture When warmed with dilute sulphuric acid hydrolysis occurs and carbonyl sulphide, COS, is formed. $HCyS + H_2O = NH_3 + COS$; whereas cyanic acid under similar condition gives carbonyl oxide, that is, carbon dioxide

§ 6 Oxidation and Reduction

This is a convenient place to recapitulate the meaning of the above terms The word "oxidation" connotates the process of combination of oxygen with an element or compound: and "reduction," the reverse operation, namely, the withdrawal of oxygen from an oxy-compound. Loss of oxygen by heat, as in the "reduction" of mercuric oxide, p 129, although it results in the removal of the oxygen from mercury, is not usually called reduction The ideas associated with oxidation and reduction have been extended to include elements other than oxygen For instance, the transformation of mercuric chloride $HgCl_2$, to mercurous chloride, HgCl, and finally to mercury by the action of stannous chloride, $SnCl_2$, are processes of reduction The stannous chloride is at the same time oxidized to stannic chloride, $SnCl_4$, thus $SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl$ The two operations—oxidation and reduction—are reciprocal in that the oxidizing agent is reduced, and the reducing agent is oxidized by the process In general, powerful oxidizing agents are readily reduced, and powerful reducing agents are readily oxidized. Similarly, the removal or addition of hydrogen is styled a process of oxidation or of reduction respectively, thus, acetylene, C_2H_2, is reduced to ethylene, C_2H_4, and ethylene is reduced to ethane, C_2H_6, by nascent hydrogen The change of a ferro- to ferri-cyanide is an oxidation process because it corresponds with a change of $FeCy_2$ to $FeCy_3$, analogous with the transformation of $FeCl_2$ to $FeCl_3$.

Oxidation is usually attended by an increase in the active valency and reduction by a decrease in the active valency of the central atom; or, as the ionic hypothesis would express it, the number of electrical charges on the ion is usually increased during oxidation, and diminished during reduction Thus, when a solution of ferric chloride is reduced to ferrous chloride by treatment with stannous chloride, Sn becomes Sn, and Fe becomes Fe But when barium oxide changes to barium peroxide there is probably no change in valency.

It is usual to say that oxidation is a process which involves the passage of a compound from a lower to a higher state of oxidation, by the addition of oxygen or of an acidic (electronegative) atom or radicle, or by the removal of hydrogen or an equivalent basic (electropositive) atom or radicle Reduction is the converse of the process of oxidation An oxidizing agent is a substance which can engender oxidation as just defined, and conversely with a reducing agent

Among the available oxidizing agents are oxygen, ozone, the peroxides, and the higher oxides as well as the unstable basic oxides of silver, gold, etc , the oxy acids (nitric, nitrous, chromic, chloric, and the other oxy-acids of the halogens) and their salts the halogens (chlorine, bromine, iodine), permanganic acid and its salts, potassium ferri cyanide, etc

Among the available reducing agents are hydrogen, unstable hydrides (hydrogen sulphide, hydrogen iodide, phosphine, arsine, stibine, etc); carbon, carbon monoxide, sulphur dioxide, and the sulphites, phosphorous acid and the phosphites, hypophosphorous acid and the hypophosphites, potassium cyanide, potassium formate, ferrous, stannous, and chromous salts, the metals sodium, potassium, magnesium, aluminium, etc These oxidizing and reducing agents have been discussed individually in earlier chapters.

Questions

1 What is the action of concentrated sulphuric acid on any five of the following substances—(a) potassium nitrate, (b) sodium carbonate, (c) charcoal, (d) potassium cyanide, (e) potassium oxalate, (f) potassium iodide, (g) copper?—*St Andrews Univ*

2 How may potassium ferrocyanide be made? How are the following made from it—potassium cyanide, carbon monoxide, potassium ferricyanide, Turnbull's Blue? Write all the equations —*Univ Pennsylvania, U S A*

3 Discuss any three of the following (a) The action of heat on ammonium chloride, (b) The displacement of zinc by copper from a solution of a zinc salt containing excess of potassium cyanide, (c) The alkalinity of aqueous sodium carbonate solution, (d) The formula of ozone —*St Andrews Univ*

4 20 c c of a solution of hydrocyanic acid mixed with excess of potash require 50 c c of decinormal solution of silver nitrate to produce faint turbidity What per cent in the liquid?—*New Zealand Univ*

5 Calculate the heat of formation of hydrogen cyanide given —$C + O_2 = CO_2 + 96\ 9$ cals, $H_2 + O = H_2O + 68\ 4$ cals, $2HCy + 5O = 2CO_2 + H_2O + N_2 + 319\ 6$ cals —*French Coll*

6 Name two oxidizing agents and two reducing agents, and explain how they may be used in connection with the salts of iron Under what conditions does the interaction occur in each case?—*Board of Educ*

7 Outline methods by which the following cuprous compounds can be obtained from copper sulphate —(a) cuprous oxide, (b) cuprous chloride, (c) cuprous hydride, (d) cuprous cyanide, and describe briefly the appearance and properties of each For what purposes is the chloride used in laboratories? Give reasons for the formula, CuCl or Cu_2Cl_2, which you assign to this substance —*Board of Educ*

CHAPTER XL

Silicon

§ 1 Silica, or Silicon Dioxide.

Silica is one of the most important compounds in the "half-mile crust" of the earth. It occurs abundantly in the mineral kingdom. and it is also common in the connective tissue of animals, fibres of vegetables, etc The so-called *kieselguhr* or "diatomaceous earth" is a mass of siliceous skeletons of dead diatoms. Silica, SiO_2, occurs in nature free and combined with various bases to form numerous mineral silicates. Free silica occurs crystalline and amorphous. There are three main types of crystalline silica: quartz, tridymite, and cristobalite.

1. Quartz.—Quartz occurs in hexagonal prisms (trigonal system) terminating in hexagonal pyramids. A single quartz crystal weighing very nearly one ton was found at Calaveras (U.S.A.) The purest varieties of quartz—called *rock crystal*—are colourless with a specific gravity 2.67, and are hard enough to cut glass The crystals are sometimes coloured with traces of various oxides Thus. manganese oxide gives *amethyst quartz*, *smoky quartz* probably owes its colour to the presence of carbonaceous matter, *milky quartz* owes its opacity to the presence of innumerable air bubbles. Quartz also occurs massive in quartzite and quartzose rocks. Quartzose sands and sandstones are also more or less impure quartz. Rock crystal was one of the first crystallized minerals to attract the attention of the early philosophers, and they believed rock crystal to be a form of ice "so hard and dry that it becomes crystal"—A. Magnus (1250) The Greek word for ice, κρύσταλλος (crystallos), has been extended to cover the whole science of crystals—crystallography Agricola (1550) reported his belief that "rock crystal is not ice, but a denser product of cold.

Crystals of quartz are sometimes found with hemihedral[1] faces inclining to the right in some specimens, and to the left in others, and, as L. Pasteur pointed out in 1860, "quartz crystals likewise separate themselves into two sets in relation to their optical properties, for one set deviates the plane of polarized light to the right, and the other set to the left, according

[1] When a crystal shows the highest grade of symmetry pertaining to its class, the crystal is said to be holo-symmetrical or *holohedral*—from the Greek ὅλος (holos), whole; ἕδρα (hedra), base or face A crystal less symmetrical may be derived from a holohedral crystal by the suppression of half its faces when it is termed *hemihedral* from the Greek ἡμι (hemi), half; or by the suppression of three-quarters of its faces, when it is termed *tetartohedral*—from the Greek τέταρτος (tetartos), a quarter

to the same laws" The former may be called right-handed, and the latter left handed quartz As in the case of tartaric acid, indicated on p 516, the two crystals are enantiomorphic The enantiomorphism of these crystals is illustrated by Fig 299

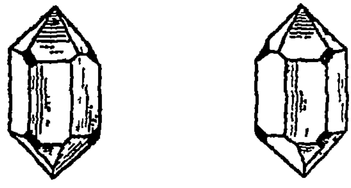


FIG 299 —Enantiomorphic Quartz Crystals

2 Tridymite —This is a second variety of crystalline silica which was discovered by G von Rath in 1868 in some andesitic rocks from the San Cristobel mountains at Pachuca (Mexico) Tridymite crystallizes in six-sided tabular crystals belonging to the triclinic system. Tridymite has been found in some meteorites It is formed when quartz is heated for a long time at about 1000° Hence tridymite is very common in silica bricks, etc which have been heated in industrial furnaces According to Day and Shepherd (1906) the transition temperature is about 800°, so that

$$SiO_2\text{quartz} \xrightleftharpoons{800^\circ} SiO_2\text{tridymite}$$

The transformation of tridymite back to quartz, below 800°, is exceedingly slow The velocity of the change is accelerated in the presence of chlorides of the alkali metals, sodium tungstate etc The specific gravity of tridymite is 2 33 as contrasted with 2 67 for quartz

3 Cristobalite —This is a third variety of crystalline silica which occurs in small octahedral (tetragonal) crystals up to about two mm. in size It was discovered in the above mentioned rocks at Pachuca The specific gravity of cristobalite is practically the same as tridymite, being nearly 2 34 Cristobalite crystals are formed in silica bricks which have been heated some time to a temperature at which quartz begins to sinter

Amorphous silica —Amorphous silica occurs in nature associated with 3 to 12 per cent of water in the mineral *opal*, which may be colourless or tinted yellowish-brown, etc, with iron oxide, organic matter, etc Chert, flint, chalcedony, jasper, contain more or less amorphous silica associated with quartz so difficult to recognize that these minerals were once thought to be amorphous silica They are said to be cryptocrystalline—from the Greek κρυπτός (cryptos), hidden

Properties of silica —Silica melts to a colourless glass—quartz glass —in the oxyhydrogen blowpipe The melting point of quartz is not well defined. Melting commences about 1600° Silica can be vaporized in the electric furnace The specific gravity of vitreous silica is about 2 22 The coefficient of thermal expansion of vitreous quartz is remarkably small—nearly 0 0000005—so that quartz glass can be very rapidly cooled without cracking For instance, quartz glass can be heated red hot in the blowpipe and plunged in cold water without fracture, under the same conditions, ordinary glass—with a coefficient of thermal expansion of 0 000008—would shatter into small fragments When heated for some time at about 1250°, the vitreous quartz passes into the crystalline condition (tridymite), and it will not then bear the sudden heating and cooling so well

Silica is reduced by carbon in the electric furnace and forms carborundum (*q v*), it is reduced by magnesium to amorphous silicon Crystalline

and vitreous silica appear to be insoluble in water and in all acids except hydrofluoric acid Fused silica is readily attacked by phosphoric acid and by the alkalies Crystalline silica is slowly attacked by aqueous solutions of alkaline hydroxides, and carbonates, but the amorphous variety is rapidly attacked Silica is also attacked by superheated water, and a small quantity may pass into solution The necessary conditions seem to prevail in deep seated cavities in the earth The water rising to the surface is cooled, and the pressure reduced Some of the dissolved silica is then deposited at the mouth of the spring as a thick jelly This afterwards changes into a hard white porous mass called *geyserite* The Great Geyser of Iceland, for instance, is surrounded by a large mound or hillock of silica with a funnel like cavity from which the geyser discharges. Similar geysers occur in the Hot Springs of New Zealand the geysers and hot springs of Yellowstone Park, U S A., etc In many cases—*e g* the mineral springs at Yellowstone Park—the alkalinity of the water facilitates the solution of the silica The alkaline silicates are decomposed by the carbon dioxide of the atmosphere and the silica is deposited as geyserite or " siliceous sinter " in the neighbourhood In general, the decomposition of the silicates by exposure to the atmosphere, or the weathering of silicates, furnishes amorphous or opaline silica

Although chemically inactive at ordinary temperatures, silica acts as a powerful acid anhydride at high temperatures, combining with the bases and many metallic oxides to form more or less fusible silicates The more fusible silicates—*e.g* lead silicate—are used in making glasses and pottery glazes Potassium and sodium silicates are soluble in water, and the aqueous solution is sold as " water glass," and the solid as " soluble glass " The powerful acid character of silica at high temperatures turns on the fact that most of the acid anhydrides—SO_3, P_2O_5, etc —volatilize at much lower temperatures, and consequently, as soon as ever so little, say, sulphur trioxide is displaced, the volatile anhydride passes away and ceases to compete with the silica for the base At lower temperatures, sulphur trioxide rapidly displaces silica from the bases when competing under equal conditions

Uses of silica —Quartz glass is used for the manufacture of elastic threads to suspend the delicate parts of electrical instruments It is made into tubes, flasks, dishes, etc Sandstone and quartzite are used for building stones, grindstones, whetstones, etc Sand or sandstone is ground with a little lime or binding clay and made into refractory bricks, " ganister bricks," " silica bricks," " Dinas bricks," etc Many varieties of quartz are shaped into ornaments and gems Diatomaceous earth —also called tripoli, kieselguhr, or (wrongly) infusorial earth—is used as a polishing powder, in the manufacture of cement, soluble glass, dynamite, and refractory bricks

§ 2 Silicic Acids

If the soluble alkaline silicates be treated with acids, an amorphous gelatinous mass called " silicic acid " is obtained This is appreciably soluble in water and in acids, and is readily dissolved by dilute solutions of the alkali hydroxides and carbonates The jelly-like mass, when dried in air, retains about 16 per cent of water, and at 100°, about 13 per cent The mass is then practically insoluble in water and acids By further

heating more and more water is expelled, thus, at 200°, about 5½ per cent of water remains, at 300° about 3 per cent, and eventually, at about 500°, anhydrous silica is formed. The dehydration curve showing the vapour pressures of "hydrates" of different composition shows no "breaks" as would probably be the case if definite hydrates were formed. If "silicic acid" which has been heated to 200° be exposed to a moist atmosphere, water is again absorbed, and the vapour pressure of the "hydrate" is greater than the original "hydrate" of the same composition. This shows that the water is probably less firmly retained by the re-hydrated silicic acid. A dilute solution of sodium carbonate—say, 5 per cent.—dissolves all the above-mentioned *silicic acids*. The rate of solution and possibly also the solubility of "silicic acid" is smaller the higher the temperature at which the hydrate has been heated. Silica which has been calcined at 1000° is dissolved with extreme slowness. Native quartz is almost insoluble in 5 per cent. sodium carbonate, but if finely powdered, appreciable quantities are dissolved in a short time.

When a solution of water glass (sodium or potassium silicate, say, Na_2SiO_3) is acidified with hydrochloric acid, some of the silicic acid separates as a gelatinous mass (hydrogel) and some remains in solution (hydrosol). If the solution be sufficiently dilute, the *silicic acid will all remain in solution along* with the excess of hydrochloric acid, and the sodium chloride formed in the reaction $Na_2SiO_3 + 2HCl \rightleftharpoons H_2SiO_3 + 2NaCl$. The hydrochloric acid and the sodium chloride can be separated from the silicic acid by dialysis (Fig. 109). To avoid the trouble of changing the water, the dialyzer illustrated in Fig. 300, can be used in place of the simpler form Fig. 109, used by Graham. In the improved apparatus a current of water is kept circulating about the outside of the dialyzing membrane. The dialyzing surface is also relatively great so that the operation is much quicker than before.

FIG. 300.—Proskauer's Dialyzer.

A 5 per cent. solution of colloidal silica can be obtained as a hydrosol, by dialysis. This solution can be concentrated by boiling in a flask until it contains about 14 per cent. of silicic acid. The solution so prepared gelatinizes, or assumes the hydrogel condition, on standing a few days. The passage of silicic acid from the sol to the gel condition is retarded by the presence of a little hydrochloric acid, or alkali hydroxide, and is accelerated by a little sodium carbonate. If the clear solution of silicic acid be allowed to evaporate *in vacuo* at about 15°, a clear transparent jelly is obtained which, when dried over sulphuric acid, has approximately the composition H_2SiO_3, that is, $SiO_2.H_2O$, and it is called metasilicic acid. An acid of the same composition has been made by dehydrating gelatinous silicic acid with 90 to 95 per cent. of alcohol. An acid of approximately the composition $SiO_2.2H_2O$, that is, H_4SiO_4, and called orthosilicic acid, has been made by dehydrating gelatinous silicic acid with absolute ether, and drying the amorphous white powder between folds of filter paper. Orthosilicic acid loses water on exposure to the air

Like sulphurous and carbonic acids, the silicic acids dissociate so readily into water and acid anhydride, SiO_2, that there is some doubt about the existence of definite hydrates Indeed, it is generally believed that the water is not "chemically combined" with the silica, p 774 The real existence of the definite hydrates just indicated is thus open to question The fact that the powders prepared by the processes just indicated have approximately a composition corresponding respectively with $SiO_2\,H_2O$ and $SiO_2\,2H_2O$ is attributed to chance Be this as it may, a large number of compounds of silica with the bases—silicates—are known, and a large number occur in nature as definite minerals, and many others have been prepared artificially These salts can be referred to unknown silicic acids

If a 1 per cent aqueous solution of sodium silicate be decomposed by hydrochloric acid two kinds of silicic acid may be obtained—α-silicic acid not precipitated by a solution of egg-albumen, and β-silicic acid which is precipitated by the same treatment The β-acid is converted into the α-acid by warming its aqueous solution Solutions of alkaline silicates of the type R_4SiO_4, R_2SiO_3, $R_2Si_2O_5$, give solutions of the α-acid, and ordinary water glass, or the silicate, $Na_2Si_4O_9$, give the β-acid. Osmotic pressure phenomena indicate that the molecular weight of the β-acid approaches 49,000, and it is accordingly inferred that the molecule is very complex

§ 3 The Silicates

Starting with orthosilicic acid, H_4SiO_4 or $Si(OH)_4$, this is supposed to pass into metasilicic acid, H_2SiO_3 or $SiO(OH)_2$, by the loss of one molecule of water These acids correspond respectively with the ortho- and meta-silicates Ethyl orthosilicate, $Si(OC_2H_5)_4$, is formed by the action of alcohol on silicofluoroform, $SiHF_3$ Among other orthosilicates, we have

$$\begin{matrix}HO\\HO\end{matrix}\!>Si<\!\begin{matrix}OH\\OH\end{matrix} \qquad \begin{matrix}NaO\\NaO\end{matrix}\!>Si<\!\begin{matrix}ONa\\ONa\end{matrix} \qquad Zn<\!\begin{matrix}O\\O\end{matrix}\!>Si<\!\begin{matrix}O\\O\end{matrix}\!>Zn$$

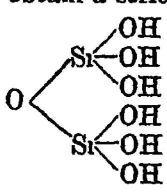
Orthosilicic acid Sodium orthosilicate Zinc orthosilicate (willemite)

Other well defined orthosilicates are olivine, Mg_2SiO_4, zircon (zirconium quadrivalent), $ZrSiO_4$, etc Among the metasilicates

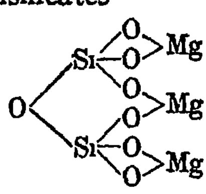
$$\begin{matrix}HO\\HO\end{matrix}\!>Si=O \qquad \begin{matrix}KO\\KO\end{matrix}\!>Si=O \qquad Ca<\!\begin{matrix}O\\O\end{matrix}\!>Si=O$$

Metasilicic acid Potassium metasilicate Calcium metasilicate (wollastonite)

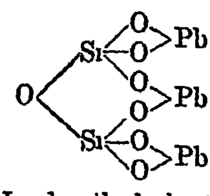
as well as enstatite, $MgSiO_3$, etc Two molecules of orthosilicic acid may be condensed into one molecule of orthodisilicic acid, $H_6Si_2O_7$, and hence we obtain a series of orthodisilicates



Orthodisilicic acid



Magnesium orthodisilicate (serpentine)



Lead orthodisilicate (barysilite)

Similarly, by the loss of one molecule of water between two molecules of metasilicic acid, the two molecules of the meta acid can be condensed

to one molecule of metadisilicic acid, $H_2Si_2O_5$. Corresponding metadisilicates are well known. Similarly, ortho and meta trisilicic acids can be derived from three molecules of the respective acids. In addition to these silicates, hydrated, acid, and basic silicates are known. Many of the double silicates of aluminium and the bases are best referred to unknown alumino silicic acids as indicated later. The system used in naming the silicates just indicated is conveniently summarized in Table LVII.

TABLE LVII.—NAMING THE SILICATES

Name	Hypothetical acid	Silicate (R^I)			
		Mono	Di	Tri	Poly-
Meta	$H_2O.SiO_2$	$R_2O.SiO_2$	$R_2O.2SiO_2$	$R_2O.3SiO_2$	$R_2O.nSiO_2$
Ortho	$2H_2O.SiO_2$	$2R_2O.SiO_2$	$2R_2O.2SiO_2$	$2R_2O.3SiO_2$	$2R_2O.nSiO_2$
Para	$3H_2O.SiO_2$	$3R_2O.SiO_2$	$3R_2O.2SiO_2$	$3R_2O.3SiO_2$	$3R_2O.nSiO_2$

Since we really know little more than the empirical formulæ of most of the silicates, the numerous attempts which have been made to classify the different silicates are more or less tentative, or speculative. The alkaline silicates are soluble in water, forming the so-called soluble glass; the other silicates are not usually soluble in water. Many of the simple silicates are attacked by hydrochloric acid, particularly if they have been roasted at a dull red heat. The silicic acid then separates as a gelatinous mass. The insoluble silicates are usually brought into solution for analysis by fusion with sodium carbonate, and the cold "cake" broken down by treatment with dilute hydrochloric acid. When the solution is evaporated to dryness, nearly all the silica separates in a form insoluble in dilute hydrochloric acid.

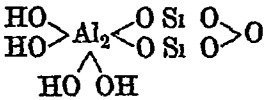
The formation of metallic silicates is well illustrated by a familiar experiment—*silica garden*. A litre beaker is filled with a solution of sodium silicate (sp. gr. 1.1) and crystals of, say, cobalt nitrate, cadmium nitrate, copper sulphate, ferrous sulphate, nickel sulphate, manganese sulphate, zinc sulphate, etc., are allowed to fall into the beaker so as to rest on different parts of the bottom. The whole is allowed to stand overnight in a quiet place, when plant-like shoots are obtained which have a form and colour characteristic of each metal.

§ 4 The Aluminosilicates

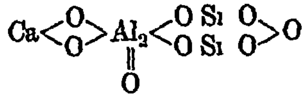
Certain compound silicates of aluminium with other bases appear to be "complex" aluminosilicates no more closely related to the silicates proper than the ferrocyanides are related to the cyanides. Just as it is convenient to refer the different silicates to more or less hypothetical silicic acids, so it is often convenient to refer many of the compound silicates to hypothetical aluminosilicic acids.

Alumino-monosilicic acid	$Al_2O_3.SiO_2.nH_2O$
Alumino-disilicic acid	$Al_2O_3.2SiO_2.nH_2O$
Alumino-trisilicic acid	$Al_2O_3.3SiO_2.nH_2O$
Alumino-tetrasilicic acid	$Al_2O_3.4SiO_2.nH_2O$
Alumino-pentasilicic acid	$Al_2O_3.5SiO_2.nH_2O$
Alumino-hexasilicic acid	$Al_2O_3.6SiO_2.nH_2O$

Thus, kaolinite, Al_2O_3 $2SiO_2$ $2H_2O$, appears to be an alumino-disilicic acid, anorthite or lime felspar CaO Al_2O_3 $2SiO_2$, the calcium salt of a similar acid, etc. Graphically, with the system indicated on p. 635, aluminium a triad, silicon a tetrad:

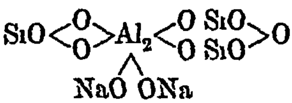


Kaolinite

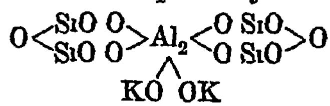


Anorthite

With natrolite, Na_2O Al_2O_3 $3SiO_2$, and leucite, K_2O Al_2O_3 $4SiO_2$, we have salts of aluminotri- and aluminotetra-silicic acids respectively:

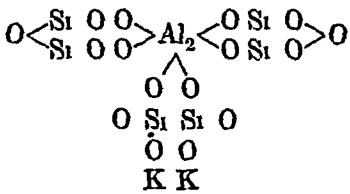


Natrolite

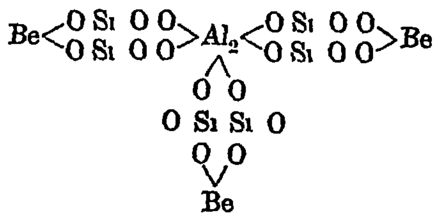


Leucite

Potash felspar, K_2O Al_2O_3 $6SiO_2$, is regarded as the potassium salt and the emerald the beryllium salt of an alumino-hexasilicic acid:



Potash felspar, or orthoclase



Emerald

Weathering of rocks.—When potash felspar and many other natural alumino-silicates are exposed to certain natural influences, they are finally converted into insoluble white crystalline or amorphous (colloidal) powder—clay, and other materials. The more important agents which facilitate the decomposition and disintegration—weathering—of the aluminium silicates are: (1) Volcanic gases (steam, hydrofluoric acid vapours, etc.); (2) Water draining from peat bogs, and coal beds. This water contains organic acids in solution. (3) Spring or rain water containing carbon dioxide, etc., in solution. As indicated above, the decomposition of silicates exposed to similar agents apparently furnishes colloidal silica—*e.g.* opal. Hence, the weathering of the alumino-silicates furnishes clay in a more or less colloidal condition.

Formation of clays.—The early stages of the decomposition—weathering—of the felspar is indicated by the apparent clouding of the crystals of felspar; the felspar becomes more and more opaque, and finally disintegrates. Consequently, granitic rocks, with felspar as a matrix, Fig. 2, disintegrate and leave behind the clay mixed with the more or less resistant varieties of mica, quartz, and other minerals which originally formed the granitic rock. The clay may be leached by streams of water from the place where it was formed, transported from the hills, and deposited at lower levels. All kinds of *debris* from the rocks and soils, etc., over which the clays are carried may be transported along with the clay. Transported clays are usually, but not always, less pure than the residual primary clays. The residual clays formed by the weathering of the less ferruginous granitic rocks, after an elaborate process of washing and settling, furnish

white *china clay*, which has very nearly the empirical composition $Al_2O_3\ 2SiO_2\ 2H_2O$ China clay is often called "kaolin," generally outside the industry The object of the washing is to separate the china clay from the unweathered quartz, mica, etc

Pottery and bricks—The term *clay* is applied industrially to a fine grained mixture of various minerals which has these qualities (1) It is plastic enough to be moulded when it is wet, (2) It retains its shape when dried in spite of a certain amount of contraction, and (3) When the moulded mass is heated to a high enough temperature it sinters together forming a hard coherent mass without losing its original contour These properties have given clays an important place—probably third or fourth—in the world's industries Clays are used in the manufacture of building bricks, tiles, firebricks, crucibles, gas retorts, sanitary goods, pottery, etc, china clay is also extensively employed for filling paper, cotton, etc

British pottery is generally made from an intimate mixture of white burning clay, with flint or quartz, and felspar or Cornish stone The mixture is moulded into the desired shape, dried, and fired between 1000° and 1200° according to the kind of ware being made This forms the so called "biscuit" body A fusible mixture—containing lead boro silicate, clay, felspar, etc, ground together to form a "slip" with water—is then spread over the surface of the "biscuit body," and the whole is refired to 900° or 1000° The melted mixture covers the surface of the "body" with a glassy film or "glaze" There are many modifications The ware may be decorated by painting coloured oxides on the biscuit body before glazing, or by painting fusible enamels on the glaze and refiring, or the glaze itself may be coloured with suitable oxides Glaze and body may be fired in one operation with or without a preliminary baking of the body There are also considerable variations in the composition of the body and glaze The chief varieties of pottery are "earthenware"—made from white burning clays, Cornish stone, and flint, "hard porcelain"—made from clays, felspar, and quartz—with or without a little lime, "bone china"—made from bone ash, clay, and Cornish stone, and the commoner varieties of pottery made from special mixtures—often local clays glazed with a mixture containing galena, etc Drain pipes are also made from local clays, which burn a buff or red colour, and glazed by throwing salt into the kiln The salt decrepitates, volatilizes, and the vapours attack the surface of the clayware, covering it with a glass like skin—*salt glaze* Tobacco pipes (unglazed) are made from siliceous clays, that is, from clays containing more or less finely divided silica Firebricks are made from refractory clays which soften at about 1650° The refractory clay is moulded by hand or machinery, and fired to about 1100°–1200° Common building bricks are usually made from less refractory clays fired at a lower temperature

Ultramarine—Occurs in nature as *lapis lazuli*, a blue, green, or violet coloured crystalline mineral It is considered to be a silicate of aluminium and sodium with some combined sulphur But its constitution is by no means understood Artificial ultramarine is a blue pigment made by calcining a mixture of china clay, sodium carbonate, charcoal, and sulphur in the absence of air The green product is washed with water, dried, mixed with sulphur, and again roasted in air until the mass has acquired

the required tint Ultramarine is decomposed by acids with the evolution of hydrogen sulphide It is used for neutralizing the yellowish tinge of sugar, cotton and linen goods, and in the laundry. It is also used as a blue pigment

Glass —As previously indicated, glass is a solidified undercooled solution of several silicates—most commonly potassium, calcium, and lead—and is made by fusing together a mixture of clean sand, limestone, or whiting or lime, sodium or potassium carbonate, and litharge or red lead in the right proportions Traces of manganese dioxide or selenium are sometimes added to neutralize the yellow or green tinge due to the presence of ferrous or ferric oxide present as impurity in the ingredients used in making the glass The mixture is melted in fireclay pots, and when the molten mass has cooled to the right temperature, a portion is collected at the end of an iron tube and brought to the desired shape by forcing it into a mould, or blowing into the tube and twisting or swinging the plastic mass of glass as required Details of the procedure vary with the particular objects being made Rapidly cooled glass is brittle and liable to fracture, hence the glass is annealed in an annealing kiln where it can be cooled as slowly as desired If cooled too slowly the glass devitrifies, *i e* crystallizes, p 167

Window glass is a soda-lime silicate This type of glass is sometimes called "soda-glass" or "soft glass," and it is used for making chemical glass ware *Window glass, plate glass,* and glass for table ware, and bottles are also made from the same constituents in different proportions and of different degrees of purity *Bohemian glass* is a potash-lime silicate, It is a hard glass and fuses only at a high temperature, hence it is used for making chemical apparatus designed to withstand high temperatures It also resists the solvent action of water better than soda glass *Jena glass* and Bohemian glass are varieties of potash-lime glass *Flint glass* is a lead potash silicate It is lustrous, and refracts light much better than other types of glass It is used for making lenses for optical purposes. Some varieties are made into artificial gems and ornamental glass *Cut glass* is a variety of lead glass which is ground or "cut" on emery or carborundum wheels Besides these special admixtures, metallic oxides may be added to colour the glass Translucent or white glass is made by the addition of bone ash, or fluorspar, or cryolite Boric acid is also used in the manufacture of glass with a high refractive index

§ 5 Carbon and Silicon Halides

We shall see, later on, that the elements carbon, silicon, germanium, tin, and lead have a family relationship They all form halides of the type CF_4, CCl_4, etc The tetrachlorides, for instance, are all liquid at ordinary temperatures, and boil

CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$
76°	59 6°	86°	113 9°	decomposes when heated

Silicon tetrafluoride, SiF_4—This gaseous compound is important It was discovered by K W Scheele in 1771 It was afterwards made by J Priestley, and its composition determined by J L Gay-Lussac and J Thénard, 1808, J Davy, 1812, and J J Berzelius, 1824 Silicon tetrafluoride is made by the direct action of fluorine on amorphous silicon.

Carbon fluoride, it may be added, is made by the direct action of the elements. Silicon fluoride is also made by the action of hydrofluoric acid upon silica or on a silicate—*e.g.* glass. $SiO_2 + 4HF \rightarrow 2H_2O + SiF_4$. The other fluorides of the family indicated above can be made by the action of hydrofluoric acid on the elements. Silicon tetrafluoride is usually made by the action of hydrofluoric acid derived from a mixture of calcium fluoride and sulphuric acid upon silica. The mixture is heated in a flask—illustrated in Fig. 301—fitted with a safety funnel containing mercury. An excess of sulphuric acid is used to absorb the water formed during the reaction.

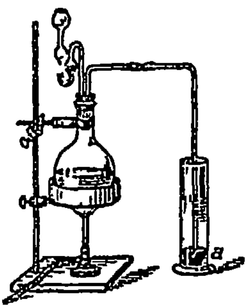


FIG. 301.—Preparation of Hydrofluosilicic Acid.

Properties of silicon fluoride.—Silicon tetrafluoride is a colourless gas with a pungent odour resembling hydrogen chloride. The density of the gas is 104.2 (oxygen = 32). This corresponds with the formula SiF_4. Silicon tetrafluoride condenses to a colourless liquid at −160° under atmospheric pressure; solidifies at −97° and melts at −77°. It can be sublimed without liquefaction at −90°. Glass is not attacked by dry silicon tetrafluoride. If the gas be passed over heated potassium it is decomposed with the separation of amorphous silicon. $SiF_4 + 4K = Si + 4KF$.

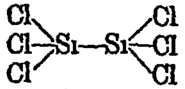
Hydrofluosilicic acid, H_2SiF_6.—If silicon tetrafluoride be passed into water, it decomposes, gelatinous silicic acid is precipitated, and hydrogen fluoride is formed: $SiF_4 + 4H_2O = Si(OH)_4 + 4HF$. The hydrogen fluoride immediately combines with a molecule of silicon tetrafluoride producing an aqueous solution of hydrofluosilicic acid. The whole reaction is written: $3SiF_4 + 4H_2O = Si(OH)_4 + 2H_2SiF_6$. In order to prevent the choking of the delivery tube by the separation of silicic acid when the silicon tetrafluoride is passed into water, it is well to let the delivery tube dip below a little mercury, *a*, Fig. 301, placed at the bottom of the vessel of water. The aqueous layer is frequently stirred to prevent the formation of channels of silicic acid through which the gas can escape into the atmosphere without coming in contact with the water. This is a good *method of making hydrofluosilicic acid*. The silicic acid is separated from the aqueous solution by filtration; the aqueous solution cannot be concentrated very much by evaporation because it decomposes into silicon tetrafluoride and hydrogen fluoride. A solid hydrate $H_2SiF_6.2H_2O$ has been prepared.

Hydrofluosilicic acid reddens blue litmus, and it is neutralized by the bases forming salts, fluosilicates. For instance, with potassium hydroxide, it forms potassium fluosilicate: $2KOH + H_2SiF_6 = K_2SiF_6 + 2H_2O$. Here the ion SiF_6'' behaves as a bivalent anion. Most of the fluosilicates are fairly soluble in water, but the potassium and barium fluosilicates are dissolved with difficulty. Hence the use of hydrofluosilicic acid in testing for barium salts, and in the estimation of potassium. Hydrofluosilicic acid is used for giving wood a stone-like surface. The wood is first soaked in lime water and then treated with hydrofluosilicic acid. The acid is also used in the paper industry, and as an antiseptic in medicine.

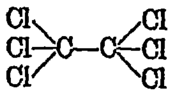
Silicon tetrachloride, $SiCl_4$.—We have seen that carbon tetrachloride, CCl_4, is the final substitution product of methane, p. 693, or of carbon disulphide by chlorine. Germanium and tin tetrachlorides—$GeCl_4$ and $SnCl_4$—are made by the action of chlorine on the elements, and lead tetrachloride, $PbCl_4$, by the action of chlorine on an hydrochloric acid solution of lead dichloride. Carbon tetrachloride cannot be made by the direct action of chlorine on carbon, but silicon tetrachloride can be made by heating silicon or silicon carbide, or an intimate mixture of carbon and silicon dioxide in a stream of chlorine: $SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$. The liquid which condenses can be freed from the excess of chlorine by shaking it with mercury, and redistilling. The colourless fuming liquid so obtained fumes in moist air. It has a vapour density and composition corresponding with $SiCl_4$. It thus resembles carbon tetrachloride. Silicon tetrachloride boils at 58.3° and freezes at −89°; carbon tetrachloride boils at 76° and freezes at −30°. Silicon tetrachloride is decomposed by water into silicic and hydrochloric acids: $SiCl_4 + 3H_2O = H_2SiO_3 + 4HCl$. Carbon tetrachloride is not acted upon by water while the other chlorides of the family are decomposed in dilute aqueous solutions if hydrochloric acid be absent. Silicon tetrachloride combines with ammonia, forming silicon tetramide, $Si(NH_2)_4$, and ammonium chloride: $SiCl_4 + 8NH_3 = 4NH_4Cl + Si(NH_2)_4$. This compound when heated forms silicon diimide, $Si(NH)_2$, and silicon nitride, Si_3N_4.

If the vapour of silicon tetrachloride be passed through a hot tube containing silicon, silicon hexachloride, Si_2Cl_6, is formed: $3SiCl_4 + Si = 2Si_2Cl_6$. Silicon hexachloride is a mobile fuming liquid boiling between 146° and 148°, and freezing at −1°. Silicon hexachloride dissociates when heated to 350°: $2Si_2Cl_6 \rightleftharpoons Si + 3SiCl_4$, and the dissociation is practically complete at 800°. If, however, the silicon hexachloride be rapidly heated to 1000°, it has not time to dissociate to any great extent in passing through 350° to 1000° and the compound is stable above 1000°. Allied phenomena have been previously studied, pp. 184, etc.

Perchlorethane, or carbon hexachloride, C_2Cl_6, is analogous with silicon hexachloride; the former boils at 187°, the latter at 147°. The relations of the two are shown graphically:



Silicon hexachloride



Carbon hexachloride

Silicon hexachloride is hydrolyzed by water forming silico-oxalic acid, $Si_2H_2O_4$, analogous with oxalic acid, $C_2H_2O_4$. The relation between these two acids is indicated graphically:

O=Si—OH
O=Si—OH
Silico-oxalic acid

O=C—OH
O=C—OH
Oxalic acid

The compounds Si_3Cl_8 and C_3Cl_8 are known; the former boils at 212°, the latter at 269°. Silicon octochloride is hydrolyzed by water, furnishing silico mesoxalic acid, $Si_3O_2(OH)_4$, analogous with mesoxalic acid, $C_3O_2(OH)_4$, graphically:

O=Si—OH
HO—Si—OH
O=Si—OH
Silico mesoxalic acid

O=C—OH
HO—C—OH
O=C—OH
Mesoxalic acid

Several other halogen compounds of silicon are known. When silicon is heated to redness in a current of dry hydrogen chloride, or when the gaseous products of the action of hydrochloric acid on copper silicide are cooled by liquid air, a compound—silico-chloroform, $SiHCl_3$—is formed, boiling at 34°. The corresponding compound of carbon—chloroform, $CHCl_3$—boils at 61°; and the corresponding compound of germanium, $GeHCl_3$, boils at 72°. Although chloroform is not hydrolyzed by water, silico chloroform with water forms leucone, $SiH(OH)_3$, also called silico-formic acid. The corresponding carbon compound is not known. Leucone is somewhat unstable, for it readily loses water, forming the compound $H_2Si_2O_3$, which is called silico-formic anhydride.

$$2H{-}Si{\lessgtr}\begin{matrix}OH\\OH\\OH\end{matrix} = 3H_2O + \begin{matrix}H{-}Si{\lessgtr}O\\ \quad\;\; >O\\ H{-}Si{\lessgtr}O\end{matrix}$$

When heated, silicoformic anhydride breaks down into silicon, hydrogen, and silica. $2H_2Si_2O_3 = Si + 2H_2 + 3SiO_2$. Probably this reaction means that silicon hydride, SiH_4, and silica are first produced, and that the former decomposes at once into its elements. A compound silicofluoroform, $SiHF_3$, can be made by the action of silicochloroform on stannic fluoride, SnF_4. It boils at −80.2°; the corresponding carbon compound—fluoroform, CHF_3—boils at 20°.

§ 6 Silicon

History.—Silicon does not occur free in nature, but, as indicated in our study of silica, numerous oxygen compounds are known. The process of manufacturing glass from silicates has been known from ancient times, and J. J. Becher (1669) believed that these silicates contained a peculiar earth which he called *terra vitrescibilis* (vitrifiable earth); this is now called "silica." It was known in the seventeenth century that Becher's vitrifiable earth does not fuse when heated alone, and that a fusible glass is formed when it is heated with other earths. O. Tachenius (1660) noticed that the vitrifiable earth had acid rather than alkaline properties; K. W. Scheele (1773) showed it to have the characteristics of a refractory acid; and J. L. M. Smithson (1811) considered it to be an acid rather than an alkaline earth. J. J. Berzelius prepared amorphous silicon in 1823; and H. St. C. Deville prepared crystalline silicon in 1854.

Amorphous silicon.—This can be made by heating potassium or sodium in an atmosphere of silicon chloride or silicon fluoride. $SiF_4 + 4K = Si + 4KF$. The brown mass so formed is washed with water and hydrofluoric acid, heated at a dull red heat, and finally washed and dried. It is also formed by heating a mixture of sodium or potassium fluosilicate with metallic potassium. $K_2SiF_6 + 4K = Si + 6KF$. The brown mass is cleaned as before. Quartz is reduced to silicon when it is intimately mixed with magnesium powder and heated. $SiO_2 + 2Mg = Si + 2MgO$.

Amorphous silicon is a dark brown amorphous powder with a specific gravity 2.35. It melts at about 1500°, and volatilizes in the electric arc. When calcined in air, a surface skin of silica is formed which protects the element from complete oxidation. Silicon ignites in chlorine at about 450°, and burns to silicon tetrachloride. If silicon be heated with hydrogen

chloride, free hydrogen and silicon tetrachloride are formed $Si + 4HCl = SiCl_4 + 2H_2$ (*cf* p 93) Silicon is insoluble in water and most acids, but it dissolves in hydrofluoric acid forming hydrofluosilicic acid $Si + 6HF = 2H_2 + H_2SiF_6$ When boiled with alkaline hydroxides it forms hydrogen and alkaline silicate as indicated on p 93

Crystalline silicon —Crystalline silicon is made by dissolving silicon in molten metals, and on cooling, part of the silicon separates from the solution in a crystalline condition By passing a stream of silicon tetrachloride vapour over aluminium previously melted in an atmosphere of hydrogen, the volatile aluminium chloride passes on, and the silicon liberated by the reaction $3SiCl_4 + 4Al = 3Si + 4AlCl_3$, dissolves in the molten aluminium As the molten aluminium cools, silicon separates in long lustrous crystals The aluminium can be separated by treatment with hydrochloric acid Crystalline silicon is also made by heating a mixture of potassium or sodium silicofluoride, or powdered silica with an excess of aluminium $4Al + 3K_2SiF_6 = 3Si + 6KF + 4AlF_3$ The silicon dissolves in the excess of molten aluminium The cold solution is treated with hydrochloric acid to remove aluminium, and with hydrofluoric acid to remove silica Silica is reduced when heated with metallic magnesium $SiO_2 + 2Mg = 2MgO + Si$, if an excess of magnesium be employed, magnesium silicide, Mg_2Si, is formed Both it and magnesium oxide can be removed by treatment with hydrochloric acid. Crystalline silicon has been made commercially by heating quartz with coke in the electric furnace $SiO_2 + 2C = 2CO + Si$ If too much coke be used, carborundum is formed Silicon so prepared is sold in metallic-looking lumps and used in the manufacture of alloys

Crystalline silicon forms dark grey opaque needle like crystals or octahedral plates (cubic system) It is hard enough to scratch glass Its specific gravity varies between 2 34 to 3, according to the temperature to which it has been heated It burns when heated in chlorine and fires spontaneously in fluorine Silicon is insoluble in acids, but dissolves in a mixture of nitric and hydrofluoric acids It melts about 1500°, and distils in the electric furnace Crystalline silicon slightly conducts electricity, amorphous silicon does not Chemically, crystalline silicon resembles amorphous silicon, but it is not so active Silicon combines with nitrogen, forming silicon nitride, and also with the metals, forming silicides Siloxicon is the trade name for a greyish-green granular powder formed by heating a mixture of silica with carbon to about 2500° in an electric furnace It varies in composition between Si_2C_2O and Si_7C_7O It is used as a refractory material when shaped into bricks, furnace linings, etc

Silicon carbide, carbon silicide, carborundum—SiC —This compound is made by fusing a mixture of coke and sand in an electric resistance furnace—estimated temperature 3500° The furnace is a large oblong box with permanent ends, and temporary sides Large carbon electrodes are fitted into the two ends, and project into the furnace Granulated coke is packed between the electrodes A mixture of sand and coke, with some salt to make the mass fusible, and some sawdust to make the mass porous, is packed about the carbon core and held in place by the side walls of loosely packed bricks The furnace is illustrated diagrammatically in Fig 302 A powerful current of electricity is sent through

the charge The change which takes place is represented by the symbols $SiO_2 + 3C \rightarrow SiC + 2CO$ The operation is over in about eight hours The furnace is then allowed to cool, the side walls are removed, and the silicon carbide removed The best grades are found nearest the core The product is crushed and treated with sulphuric acid to remove impurities, it is then washed, dried, and graded according to size

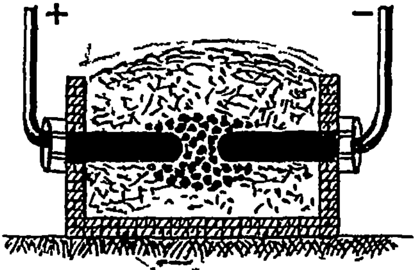


FIG 302 —Carborundum Furnace (Diagrammatic)

Carborundum crystallizes in hexagonal plates when pure, it may be transparent and colourless, or vary in tint from emerald green to brown or black The latter varieties are most common The specific gravity is 3 2 It is not attacked by acids —even hydrofluoric acid It is decomposed by fusion with alkaline hydroxides It is nearly as hard as the diamond, and accordingly is largely used as an abrasive powder and made into whet stones, hones, grinding wheels, polishing cloths, etc It is also very refractory, and when mixed with clay has special uses as a refractory material for protecting furnace walls, etc

Atomic weight —The atomic weight determined by the analysis of silicon tetrachloride, silicon tetrabromide, etc, by different experimenters, lies between 27·95 and 28 38, the best representative value is taken to be 28 3, if oxygen be 16, and this number corresponds with the molecular weight deduced from the vapour densities of the volatile compounds of silicon by Avogadro's hypothesis Dulong and Petit's rule does not apply so well unless the specific heat be taken at 300°, 0 2032

§ 7 Hydrogen Compounds of Silicon

There are three compounds of silicon and hydrogen silicon-methane or gaseous silicon hydride, SiH_4, corresponding with methane, CH_4, silico-ethane or liquid silicon hydride, Si_2H_6, corresponding with ethane, C_2H_6, and silico acetylene or solid silicon hydride, Si_2H_2, corresponding with acetylene, C_2H_2.

Silico-methane, SiH_4, or silicane —This gas is most conveniently made by the action of concentrated hydrochloric acid on magnesium silicide [1] whereby hydrogen gas containing 4 or 5 per cent of silicane and a trace of silico ethane is formed The latter is spontaneously inflammable in air, the former is not Hence the gas prepared by the above described process is spontaneously inflammable in air This property can be illustrated by the method employed with phosphine, Fig 217 The hydrochloric acid is placed in the flask, and the flask is filled with hydrogen gas, the current of hydrogen is shut off, and the magnesium silicide is dropped into the acid. The bubbles of gas ignite as they rise to the surface of the water, forming rings of silicon dioxide

[1] Magnesium silicide, Mg_2Si, is made by heating sand with an excess of magnesium powder or by fusing together 40 parts by weight of anhydrous magnesium chloride with sodium fluosilicate, 35; sodium chloride, 10, and sodium, 20

By passing the dried gases from the magnesium silicide and the acid through a tube surrounded by liquid air, both the SiH_4 and the Si_2H_6 are condensed to liquids By fractional distillation of the condensed mass at −10°, silico-methane is obtained as a colourless gas, not spontaneously inflammable at atmospheric pressure, but inflammable in air if slightly warmed or subjected to reduced pressure Silico-methane burns with a bright flame, forming silica and water $SiH_4 + 2O_2 = SiO_2 + 2H_2O$ When passed into alkaline solutions it decomposes, forming alkaline silicates and hydrogen $SiH_4 + 2KOH + H_2O = K_2SiO_3 + 4H_2$ The gas liquefies at −11°, and so solidifies at about −200° When heated 400° it decomposes into its elements, amorphous silicon and hydrogen $SiH_4 = Si + 2H_2$

Silico-ethane, Si_2H_6—Hydrogen silicide remains as a liquid when the silico-methane has been distilled from the liquefied gases obtained by the action of hydrochloric acid on magnesium silicide, as described above It is a colourless liquid, boiling at 52°, and solidifying at −138° It can be heated to 100°, in the absence of air, without decomposition, but at 200° it decomposes into its elements hydrogen and amorphous silicon $Si_2H_6 = 3H_2 + 2Si$ It is spontaneously inflammable in air, burning to water and silica Like silico-methane, this compound reacts vigorously with free halogens

Silico-acetylene, Si_2H_2—Solid silicon hydride is said to be formed when calcium silicide[1] is decomposed by hydrochloric acid $CaSi_2 + 2HCl = Si_2H_2 + CaCl_2$ It is a yellow crystalline solid The hydrides of silicon are not very stable Like many of the other hydrides, they act as reducing agents Thus silico-methane reduces silver nitrate with the separation of silver and silicon $SiH_4 + 4AgNO_3 = 4HNO_3 + 4Ag + Si$ Copper sulphate is not so easily reduced as silver nitrate, and a compound of copper and silicon—copper silicide—Cu_2Si, is formed $SiH_4 + 2CuSO_4 = Cu_2Si + 2H_2SO_4$ The more stable methane does not act like silico-methane Acetylene, it will be remembered, forms acetylides or carbides with silver nitrate and copper sulphate Many of the less stable hydrides—like silicon hydride, hydrogen sulphide, and hydrogen iodide—reduce in virtue of the hydrogen liberated during their decomposition, other hydrides reduce by the direct oxidation of their elements Thus, with arsenic hydride and silver nitrate, as previously described, arsenious acid and silver are formed during reduction

Questions.

1 Explain thoroughly how quartz may be put into solution and further treated so as to recover it as silica What experimental evidence have we that arsenic is an amphoteric element ?—*Princeton Univ, U S A*

2 Describe the *preparation, properties*, and reactions of the compounds of silicon with hydrogen, with chlorine, and with fluorine —*Aberdeen Univ*

3 How can (*a*) silicon, (*b*) silicon carbide be obtained from sand, and for what purpose are these substances used ? How can silicon chloride be obtained from silica, and converted into silica ?—*Sheffield Univ*

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[1] Calcium silicide Made by heating lime, silica, and carbon in an electric *furnace*

4 Compare and contrast the elements carbon and silicon by a discussion of their analogous inorganic compounds —*Sheffield Univ*

5 Explain the meaning of the term "anhydride" Describe the preparation of sulphur dioxide, chromium trioxide, and silicon dioxide, and the experiments by which you would prove each to be an anhydride —*London Univ*

6 What is the composition of felspar, calcspar, fireclay, and fluorspar? From which of these and by what process could you produce silica?—*Board of Educ*

7 Orthoclase felspar has the composition K_2O Al_2O_3 $6SiO_2$ Explain the methods by which the following substances could be obtained from it in a state of purity: alumina, potassium chloride, potash alum, silica —*Board of Educ.*

CHAPTER XLI

Tin, Lead, and some Related Elements

§ 1. Germanium.

In 1885 Weisbach discovered a silver mineral—*argyrodite*—in a mine at Freiberg (Saxony) C Winkler analyzed the mineral, but found his analysis to be about 7 per cent too low

Silver	Sulphur	Ferrous oxide	Zinc oxide	Mercury	Total
74 72	17 13	0 66	0 22	0 31	93·04

Winkler traced the discrepancy to the presence of 6 93 per cent of a new element, precipitated as sulphide in the "hydrogen sulphide group" This element he called germanium from the Latin name *Germania* The new element proved to be bi- and quadri-valent The compounds corresponding with bivalent germanium resemble the compounds of silicon and carbon, and compounds corresponding with quadrivalent germanium resemble tin and titanium compounds The analysis and vapour density of germanium tetrachloride correspond with an atomic weight 72 5 (oxygen = 16) This number agrees roughly with the atomic weight calculated from the specific heat 0 08 by Dulong and Petit's rule Neglecting the small admixtures of iron, zinc, and mercury, the analysis of argyrodite thus corresponds with $3Ag_2S \cdot GeS_2$.

§ 2 Tin

History —Discoveries of tin in Egyptian tombs show that the metal was fairly common in olden times It is not certain if the Hebrew word "bedil" in the Pentateuch, translated by the Greek word κασσίτερος (cassiteros), and by the Latin word *stannum*, really means tin. The word "stannum" appears to have been used by the Romans to designate certain alloys containing lead. It is not certain whether the Phœnicians obtained their tin from India, Britain, or Iberia The resemblance between the Sanscrit word "castira" and the Greek "cassiteros" has been used as an argument in favour of the Indian origin of Phœnician tin Pliny states that "cassiteron" was obtained from "Cassiterides (British Isles) in the Atlantic Ocean" This no doubt refers to the tin then obtained from the Cornish mines The Romans appear to have distinguished lead from tin by calling lead "plumbum nigrum," and tin "plumbum candidum." The word "stannum" was later restricted to tin proper The alchemists called tin "Jupiter," and represented this metal by ♃, the symbol for the planet Jupiter.

Occurrence.—There are several reports of the occurrence of metallic tin in nature. Practically, *tinstone* or *cassiterite* is the sole source of commercial tin. This mineral occurs in tetragonal crystals coloured brown or black by impurities, chiefly iron. Cassiterite is stannic oxide, SnO_2, contaminated with more or less arsenical pyrites, copper pyrites, tungstates, and various metallic sulphides. "Lode" or "vein" tin is cassiterite which is obtained from veins or lodes in primary deposits; while "stream" tin is cassiterite from alluvial secondary deposits where it occurs in more or less rounded lumps. The miners speak of tinstone as "tin" or "black tin" to distinguish it from the metal which is called "white tin". The complex sulphide ore, *stannite*, or *tin pyrites*, is a sulphide of copper, tin, iron and sometimes zinc. It is comparatively rare. About one third of the world's output of tin is produced in the Malay peninsula. Tin is also produced in the Malay archipelago, Bolivia, Australia, Cornwall, South Africa, Bohemia, and Saxony, etc.

Extraction.—The ore is first concentrated by washing away the earthy impurities. The high specific gravity of tinstone—6.8 to 7.0—enables this to be done without much trouble, as in the case of washing gold (*q.v.*). This process usually works well with stream tin; but vein tin usually requires more complex treatment. The crushed ore is first washed to remove earthy matters. The arsenic and sulphur are removed by an "oxidizing roast." The tungsten and the residue left after the calcination of the pyrites are removed by passing the calcined ore through the intense magnetic field of an "electro-magnetic separator."

The extraction of tin involves the reduction of the ore in a blast furnace or in a reverberatory furnace. Thus the "concentrated" ore—tinstone—is heated with coal in a reverberatory furnace. The oxide is reduced: $SnO_2 + 2C = 2CO + Sn$. The molten tin which collects on the bottom of the furnace is drawn off and cast into ingots or blocks—block tin—which contain about 99.5 per cent. of metallic tin. The slag obtained in this operation is also worked up to recover the 20 to 40 per cent. of metal it contains.

Refining tin.—Tin is refined by heating it, at a temperature as little as possible above the melting point of the metal, on the sloping hearth of a reverberatory furnace. The tin flows down the hearth and leaves the oxidized metallic impurities as "refinery dross" behind. This tin may be further purified by stirring the molten metal with a billet of wood. The metal is agitated by the bubbling of the rising gases, and this continually exposes fresh portions of the molten metal to the oxidizing action of the air. The impurities which collect on the surface as a "dross" are skimmed off. The refinery drosses containing a large percentage of tin are re-smelted with the ore.

Tin is recovered from scrap tin, tin plate, etc., by treating these materials with some solvent, *e.g.* chlorine. Electrolytic methods of extraction have not been very successful.

Properties.—Tin is a white lustrous metal with a pale blue tinge. The metal retains its lustre unimpaired by exposure to air. The metal is soft enough to be cut with a knife, but it is harder than lead, and not so hard as zinc. Tin is very ductile, for it can be beaten into foil—tinfoil—and drawn into wire. The ductility of tin is greatest at about 100°; at 200° the metal is brittle enough to be pulverized into powder. Tin shows a

marked tendency to crystallize on solidification If a bar of tin be bent, it emits a low crackling noise—"tin cry"—said to be due to the rubbing of the crystal faces upon one another If the surface of a block of tin be treated with warm dilute aqua regia, the surface of the metal immediately assumes a crystalline appearance The crystals are best shown by cooling molten tin in a crucible until part has solidified, and pouring out the liquid portion The walls of the crucible will be lined with crystals of tin Tin appears to be dimorphous, for electrolytic tin—*i e* tin deposited from a solution by the electrolysis of a tin salt—and malleable tin, form tetragonal crystals, while the "brittle" tin, mentioned above, is rhombic. Tetragonal tin passes into the rhombic form between 170° and 200° Tin melts at 232°, and boils at about 2275° A perceptible volatilization occurs at 1200° The metal takes fire when heated between 1500° and 1600°, burning with a white flame to stannic oxide When the metal is heated just above its melting point in air for some time, it forms a yellowish-white scum which is stannic oxide

Grey tin—When cooled to a low temperature tin crumbles to a grey friable powder Several cases have been reported where tin, during an exceptionally cold winter, has crumbled to powder, for instance, A L Erdmann (1851) noticed some tin organ-pipes crumble to powder The disease is called the "tin pest" Grey tin appears to be a third allotropic modification of the element

	Rhombic tin	$\overset{170°}{\rightleftarrows}$	Tetragonal tin	$\overset{18°}{\rightleftarrows}$	Grey tin
Specific gravity	7 25		6 55		5 8
Specific heat	0 0525		—		0 0510

The transition temperature is 18° Hence, excepting in warm weather, all ordinary white tin is in a metastable condition E Cohen has pointed out that the speed of the transformation is very slow at ordinary temperatures, but it proceeds with a maximum velocity at −48°, especially if the tin be in contact with an alcoholic solution of "pink salt," $SnCl_4 \, 2NH_4Cl$ At lower temperatures, the velocity again slows down If a piece of tin which has already commenced to change be allowed to remain in contact with a piece of ordinary white tin, the unchanged tin is more quickly affected with the "disease"

The action of acids and alkalies—Tin dissolves slowly in dilute hydrochloric acid, and rapidly in the concentrated acid, forming stannous chloride, $SnCl_2$, and hydrogen $Sn + 2HCl \rightarrow SnCl_2 + H_2$ Tin is but slowly attacked by cold sulphuric acid, but the hot concentrated acid dissolves the metal, forming stannous sulphate and sulphur dioxide $Sn + 2H_2SO_4 \rightarrow SnSO_4 + SO_2 + 2H_2O$ The action of nitric acid depends upon the temperature and concentration of the acid With cold dilute nitric acid, stannous nitrate, $Sn(NO_3)_2$, is formed $4Sn + 10HNO_3 = 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3$, with possibly a little stannic nitrate, $Sn(NO_3)_4$ With nitric acid of specific gravity 1 24, meta-stannic acid is the chief product of the action Pure nitric acid is practically without action on the metal Boiling alkaline hydroxides form alkaline stannates, *e g* K_2SnO_3, and hydrogen $Sn + 2KOH + H_2O \rightarrow K_2SnO_3 + 2H_2$

Atomic weight of tin—The combining weight of tin has been determined by the analysis or synthesis of the oxide, chloride, bromide, sulphide, and the potassium and ammonium stannichlorides The best available numbers show that this constant probably lies somewhere between 118 98

and 119.10 The best representative value is taken to be 119—oxygen = 16 The vapour density of the volatile compounds of tin, observations on the isomorphism of stannic and titanic oxides, and the specific heat, 0.055, by Dulong and Petit's rule, all point to this number 119. as the atomic weight of tin

Uses.—The resistance of tin to ordinary corrosive agents is utilized in protecting iron from rusting, "tin plate" is made by dipping thin sheets of steel into molten tin, whereby the steel is coated with a thin film of tin The plated tin so made is used in the manufacture of tin cans, and similar articles. Copper coated with tin is also used for cooking vessels Tin amalgam is used in coating mirrors.

Alloys.—Many useful alloys contain tin The addition of tin to lead lowers the melting point of lead, and the addition of lead to tin lowers the melting point of the tin Tin melts at 232°, and lead at 327°, an alloy of 37 per cent lead with 63 per cent of tin melts at the eutectic temperature 180°, as indicated in Fig. 303 "Common solder" has one part of tin to one part of lead but solders generally vary from 66 to 33 per cent of tin "Pewter" is a tin-lead alloy containing 75 per cent of tin with 25 per cent of lead It will be observed that an alloy of two metals or a salt solution may appear to have two freezing points (1) the temperature at which an excess of one constituent freezes along the lines *AO*, *OB*, Fig. 303, and (2) the temperature at which the eutectic freezes *en bloc* During the cooling of plumber's solder, for instance, say tin 40, lead 60 solid lead begins to separate at 240°, and continues separating until the mother liquid contains 37 per cent of lead, when the whole mass solidifies Between these two temperatures, 180° and 240°, the cooling alloy seems to be in a "pasty" condition, and this enables the plumber to "wipe" a joint being made with such an alloy

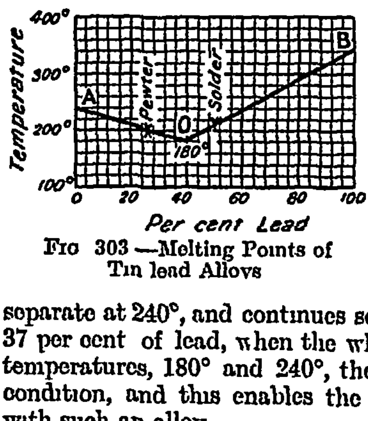


FIG 303.—Melting Points of Tin lead Alloys

§ 3 Stannous Oxide and Hydroxide

When stannous chloride, $SnCl_2$, is dissolved in an excess of water, a white precipitate of stannous oxychloride, Sn(OH)Cl, is formed $SnCl_2 + H_2O \rightleftharpoons Sn(OH)Cl + HCl$ If stannous chloride be treated with an alkali, say sodium carbonate, or sodium hydroxide, stannous hydroxide, $Sn(OH)_2$, is precipitated When heated in a current of carbon dioxide, stannous hydroxide forms black stannous oxide, SnO, which, when heated in air, burns to stannic oxide, SnO_2 Stannous hydroxide is insoluble in ammonia, but it readily dissolves in alkaline solutions, forming stannites, *e.g.* potassium stannite $Sn(OH)_2 + 2KOH \rightleftharpoons Sn(OK)_2 + 2H_2O$ Hence the stannites are to be regarded as salts of stannous acid, H_2SnO_2, which may be simply stannous hydroxide Basic stannites of the type HOSn(OK) have been isolated By the slow evaporation of alkaline solutions of the stannites, crystals of SnO can be obtained If much alkali be present, or if the solution be boiled, metallic tin separates and alkali stannates,

K_2SnO_3, are formed $2KHSnO_2 = K_2SnO_3 + Sn + H_2O$ Stannous hydroxide is converted into stannous salts when treated with acids, and consequently, stannous hydroxide exhibits both acidic and basic properties

§ 4 Stannic Oxide and Hydroxide

If an acidified solution of stannous chloride, $SnCl_2$, be exposed to the air, oxygen is absorbed, and stannic hydroxide is precipitated $2SnCl_2 + O_2 + 6H_2O \rightarrow 2Sn(OH)_4 + 4HCl$ Possibly stannic chloride is first formed $2SnCl_2 + O_2 + 4HCl \rightarrow 2SnCl_4 + 2H_2O$; and this latter is hydrolyzed by the water $SnCl_4 + 4H_2O \rightleftharpoons Sn(OH)_4 + 4HCl$ The stannic hydroxide is precipitated by ammonia, alkaline hydroxides, carbonates, ammonium nitrate, sodium sulphate, etc, from solutions of stannic salts $SnCl_4 + 4KOH \rightleftharpoons 4KCl + Sn(OH)_4$ Stannous chloride is hydrolyzed by water with the production of the same hydroxide If the precipitate be dried in air, it has the empirical composition H_4SnO_4, or $Sn(OH)_4$, and if dried over concentrated sulphuric acid, the empirical composition H_2SnO_3, or $SnO(OH)_2$ Consequently H_4SnO_4, that is, $Sn(OH)_4$, is to be regarded as ortho-stannic acid, and H_2SnO_3, or $O{=}Sn{=}(OH)_2$, as meta-stannic acid Stannates corresponding with K_2SnO_3, analogous with the carbonates, can be made by heating solutions of, say, stannic chloride with an alkaline carbonate

When metallic tin is treated with hot nitric acid (specific gravity 1 3) stannic hydroxide with the empirical formula $Sn(OH)_4$ is formed, and this when dried in air has the empirical formula H_4SnO_4, and if dried over sulphuric acid it has the empirical formula $SnO(OH)_2$ The stannic acids formed by these two different processes differ essentially in their behaviour towards many reagents For convenience, the stannic acid formed by the action of alkalies on solutions of stannic chloride is called α-stannic acid, and the acid produced by the action of nitric acid on the metal is called β stannic acid or "metastannic acid." Some of the differences between the two varieties are as follows

TABLE LVIII —PROPERTIES OF THE METASTANNIC ACIDS

α Metastannic acid	β-Metastannic acid
Salts dissolve in water easily and are not decomposed More basic than the β acid	Salts dissolve in water with difficulty and form insoluble basic salts and free acid Less basic than the α acid
When moist, dissolves readily in nitric acid	Insoluble in nitric acid
Soluble in dilute sulphuric acid and the solution does not gelatinize when boiled	Insoluble in sulphuric acid even if concentrated
Easily soluble in hydrochloric and the solution remains clear when boiled	Unites with hydrochloric acid forming a substance insoluble in acid but soluble in water The aqueous solution gelatinizes when boiled

Both varieties dissolve in caustic alkalies and in alkaline carbonates, and when reprecipitated by the addition of acids, the precipitates retain

the properties they had before dissolving in the alkalies. J. J Berzelius observed this peculiarity of the stannic acids in 1811–1823 Berzelius found that both oxides had the same ultimate composition, and the fact was regarded at the time as an "interesting example," showing that "identity of composition does not correspond with identity of properties." An explanation of the difference between the two acids is not known with certainty It is generally supposed that the β acid—$(H_2SnO_3)_5$ or $Sn_5O_5(OH)_{10}$—is a polymerized form of the α acid—H_2SnO_3. If the β acid be treated with concentrated hydrochloric acid for a short time, a compound $Sn_5O_5Cl_{10}$ is formed which is insoluble in hydrochloric acid. This substance is soluble in water with the formation of the so called β-stannic chloride or stannyl chloride $Sn_5O_5Cl_2(OH)_8$ If the aqueous solution be boiled, the β acid is reprecipitated $Sn_5O_5Cl_2(OH)_8 + 2H_2O = 2HCl + Sn_5O_5(OH)_{10}$, and if the aqueous solution be treated with hydrochloric acid, a precipitate corresponding with $Sn_5O_5Cl_4(OH)_6$ is formed. While tartaric acid prevents the precipitation of stannic hydroxide from stannic chloride solutions by ammonia, the precipitation is not prevented from solutions of β stannic chloride

These peculiarities are explained on the assumption that the two isomeric stannic acids have the constitutional formulæ

$$\begin{matrix}{HO \atop HO}\!>\!Sn\!<\!{OH \atop OH} & O{=}Sn\!<\!{OH \atop OH} & {HO \atop HO}\!>\!Sn\!<\!{O-Sn(OH)_2-O-Sn(OH)_2 \atop O-Sn(OH)_2-O-Sn(OH)_2}\!>\!O \\ \text{Orthostannic acid} & \alpha\ \text{Metastannic acid} & \beta\ \text{Metastannic acid}\end{matrix}$$

When treated with hydrochloric acid, the hydroxyl (OH) groups are replaced by chlorine, and the resulting compound, when treated with water, is more or less completely hydrolyzed As indicated above, if the β acid is boiled for a long time with concentrated hydrochloric acid, or concentrated alkaline hydroxide, it is gradually converted into the α-acid, and conversely, the α acid is gradually changed into the β acid at ordinary temperatures, but more rapidly on boiling Thus $5SnCl_4 + 13H_2O = 18HCl + Sn_5O_5Cl_2(OH)_8$ An aqueous solution of β stannyl chloride, $Sn_5O_5Cl_2(OH)_8$ gives a precipitate of β stannyl sulphate with sulphuric acid or potassium sulphate β stannic acid unites with alkalies, forming β stannates, *e g* potassium β stannate, $K_2Sn_5O_{11}\,4H_2O$ An excess of alkali precipitates the β stannates Hence β stannic acid exhibits both acidic and basic characteristics. Both stannic acids redden blue litmus, both can be obtained in a colloidal condition by the dialysis of solutions of the corresponding stannates acidified with hydrochloric acid.

An idea is growing in the minds of those who have specially studied the stannic acids that the essential difference between the two varieties is size of grain, that the particles of the α acid are the smaller and of the β acid the larger, and that there are not two distinct and well defined α- and β stannic acids, since a continuous gradation of forms intermediate between the two varieties can be made by varying the temperature of precipitation

Stannic oxide, SnO_2.—When the stannic acids are calcined, stannic oxide, SnO_2, is formed as a white powder which appears yellow when hot. Stannic oxide is also formed as a white powder by the combustion of tin If stannic chloride be heated in a current of steam, glistening rhombic crystals of stannic oxide are formed isomorphous with brookite, TiO_2

As previously indicated, stannic oxide occurs in nature in tetragonal crystals of cassiterite which are usually black in colour owing to the presence of impurities These crystals are isomorphous with rutile, TiO_2 These crystals also separate on cooling a fused solution of stannic oxide in borax When stannic oxide is strongly heated with phosphoric acid, crystals of stannic oxide isomorphous with anatase, TiO_2, are formed Hence stannic and titanic oxides are isotrimorphous. Stannic oxide is insoluble in acids and aqueous solutions of the alkalies, but it forms α-alkali stannates when fused with sodium or potassium carbonate or hydroxide Silica behaves in a similar manner

§ 5 Lead

History —Lead was known to the ancient Egyptians It is mentioned several times in the Old Testament It appears to have been confused with tin (*q v*), and Pliny seems to have distinguished between *plumbum nigrum* (black lead) and *plumbum album* or *plumbum candidum* The ancient Romans used lead for making water-pipes, and some lead compounds were used as cosmetics, and as paint The alchemists connected lead with the slow-moving planet Saturn, and accordingly represented lead by a scythe ♄, the symbol for Saturn

Occurrence —Small quantities of metallic lead are occasionally found in nature In combination with sulphur, lead occurs as sulphide, *galena*, PbS This is the most abundant ore of lead Commercial lead is obtained almost exclusively from galena Lead carbonate, *cerussite*, $PbCO_3$, is not uncommon Lead sulphate, $PbSO_4$, occurs as *anglesite*, lead chromate, *crocosite*, $PbCrO_4$, lead molybdate, *wulfenite*, $PbMoO_4$, lead phosphate, *pyromorphite*, $PbCl_2 \cdot 3Pb_3(PO_4)_2$, lead chloride, *matlockite*, $PbCl_2$ Lead ores come from England, United States, Germany, Mexico, Spain, New South Wales, South America, etc

Extraction —The galena is roasted in a current of air at a low temperature in a reverberatory furnace, so that one part of the lead sulphide, PbS, is oxidized to lead monoxide, PbO, and another part is oxidized to lead sulphate $2PbS + 3O_2 = 2PbO + 2SO_2$, $PbS + 2O_2 = PbSO_4$ The mixture of lead sulphide, lead sulphate, and lead monoxide so obtained is heated to a higher temperature with the air "shut off" The sulphide reacts with the sulphate and the lead monoxide, forming metallic lead $PbSO_4 + PbS = 2Pb + 2SO_2$, and $2PbO + PbS = 3Pb + SO_2$, and towards the end of the operation, when the lead sulphide begins to fuse $PbS + 3PbSO_4 = 4PbO + 4SO_2$ In dealing with ores low in lead, *e g* some Spanish ores, the ore is sometimes reduced by heating with iron, or a mixture of iron ore and coke Metallic lead and iron sulphide are formed $PbS + Fe = Pb + FeS$

The lead made by these processes usually contains antimony, tin, copper, etc These impurities make the lead hard and brittle A large proportion can be removed by heating the metal in a shallow flat-bottomed reverberatory furnace whereby most of the impurities are oxidized before the lead, and rise to the surface as a scum This operation is known as "softening lead" The silver is usually extracted by Parkes' process

Properties of lead —Lead is a bluish grey metal with a bright metallic lustre when freshly cut, but the lustre soon disappears in ordinary air.

Perfectly dry air, and air free water, have no action on the metal, but if moist air be present, or if the metal be immersed in aerated water, lead is soon covered with a film, probably an oxide, and this is ultimately converted into a basic carbonate. Lead is soft enough to be cut with a knife and scratched with the finger nail. It leaves a grey streak when drawn across paper. Small traces of impurity—antimony, arsenic, copper, zinc—make the lead much harder. Lead is not tough enough to be hammered into foil or drawn into wire, but it can be pressed into pipes, or rolled into thin sheets or foil. Lead filings under a pressure of about 13 tons per square inch form a solid block, and the metal seems to liquefy under a pressure of about 33 tons per square inch. The specific gravity of lead varies from 11.25 to 11.4 according as the metal is cast or rolled. Lead melts at 326°, and boils at about 1525°. When cooled slowly, the molten metal forms a mass of octahedral crystals (cubic system). The crystal line nature of the metal is shown by the electrolysis of a lead salt. Lead is also deposited as an "arborescent" mass of crystals—called a "lead tree"—when a strip of iron or zinc is suspended in a solution of a lead salt.

Lead is rapidly dissolved by nitric acid, but is little affected by dilute hydrochloric or dilute sulphuric acid in the cold, because a crust of insoluble lead chloride or sulphate is formed on the surface, and this protects the metal from further action. Powdered lead is quickly dissolved by boiling concentrated hydrochloric or sulphuric acid. Organic acids—acetic acid (vinegar)—also act as solvents for metallic lead. Hence vessels plated with tin containing lead, if used for cooking purposes, may contaminate the food with poisonous lead compounds. Water containing sulphates and carbonates in solution forms a coating on the surface of lead which prevents further action. Lead is attacked by water holding ammonium salts and carbon dioxide in solution. In the latter case, a soluble acid carbonate may be formed. All lead salts are poisonous, and if the water supply of a town be pure enough to attack lead, it is sometimes necessary to filter the water through limestone or chalk. The water then takes up enough carbonates to form a film on the interior of the lead pipes which protects the lead from further action.

Atomic weight of lead.—The combining weight of lead has been determined by the synthesis of lead nitrate and lead sulphate from metallic lead, by the analysis of lead chloride, etc. If oxygen be 16, the best determinations of the combining weight of lead vary between 206.8 and 207.6. The best representative value is supposed to be 207.1. This agrees with the result by Dulong and Petit's method of approximation since the specific heat of lead is 0.0309, and $6.4 \div 0.0309 = 207.1$. The vapour density of the volatile lead compounds also corresponds with the atomic weight 207.1. The vapour density of metallic lead between 1870° and 2000° shows that the molecule is monatomic.

Uses.—Lead is largely used in the arts on account of the ease with which it can be worked, cut, bent, soldered, and on account of its power of resisting attack by water and many acids. It is used in the manufacture of pipes for conveying water, for the manufacture of sheaths for electric wires, sheets for sinks, cisterns, and roofs, lead chambers for sulphuric acid works, evaporation pans in chemical works, etc. It is used in making bullets, shot, accumulator plates, etc. Type metal, solder, pewter, and fusible alloys contain much lead. These alloys have been previously discussed

§ 6 Lead Monoxide and Hydroxide.

The dull grey iridescent coating which is formed on the surface of lead melted at a low temperature is supposed to be lead suboxide, Pb_2O [1] If this scum be continuously removed, and again heated to a low temperature in air so as to avoid fusion, a yellow powder of lead monoxide, PbO, sometimes called massicot is formed. If this oxide be fused it forms, on cooling, a buff-coloured crystalline mass of lead monoxide, or litharge, PbO If slowly cooled the oxide has a reddish tint, and if rapidly cooled, a yellow tint It is thought that there are two modifications of lead monoxide—yellow and red, the latter being the stable form at ordinary temperatures Litharge is commonly made by the cupellation of lead. Large quantities of lead monoxide are used in preparing oils, and varnishes, and in making flint glass

Lead monoxide fuses at 877°, and it is volatile at a red heat Its specific gravity is 9 36 Lead monoxide is slightly soluble in water probably forming lead hydroxide, $Pb(OH)_2$, sufficient lead hydroxide is dissolved to give the water an alkaline reaction Lead hydroxide is best made by the addition of alkali to a lead salt The composition of the precipitate depends upon the conditions of precipitation The hydroxides $2PbO\ H_2O$ and $PbO\ H_2O$ have been reported. The precipitate is soluble in an excess of alkali hydroxide forming plumbites Potassium plumbite, $Pb(OK)_2$, for instance, is formed when potassium hydroxide is used The precipitate is insoluble in ammonia When heated to 145°, the hydroxide passes into the oxide Both oxide and hydroxide dissolve in acids forming lead salts The formation of plumbites illustrates the acidic nature of lead monoxide, and the formation of lead salts, and the alkalinity of aqueous solutions of lead hydroxide, show the basic properties of this oxide Hence lead monoxide is an amphoteric oxide

§ 7 Lead Sesquioxide and Red Lead

Lead sesquioxide, Pb_2O_3—This oxide is an orange yellow powder formed when lead hydroxide, in alkaline solution, is treated with an oxidizing agent—hypochlorites, chlorine, bromine, hydrogen peroxide, potassium persulphate—$2PbO + NaOCl = NaCl + Pb_2O_3$ When heated, lead sesquioxide forms lead monoxide and oxygen Acids, say nitric acid decompose it into lead monoxide and lead dioxide—the former dissolves in the acid forming lead nitrate With concentrated hydrochloric acid, lead sesquioxide behaves like a peroxide furnishing chlorine gas $Pb_2O_3 + 6HCl = 3H_2O + 2PbCl_2 + Cl_2$

Lead tetroxide, minium, red lead, Pb_3O_4—Red lead is formed by heating lead monoxide or white lead in air between 470° and 480° It is a scarlet powder The hot powder acquires a deeper and deeper tint as time goes on, then it appears to become violet, and finally black On cooling the original red powder appears The tint of red lead is determined largely

[1] The same oxide is made by heating lead oxalate to about 300° in a glass vessel $2PbC_2O_4 = CO + 3CO_2 + Pb_2O$ This oxide burns to PbO when heated in air, and if heated to a high temperature alone, it passes into lead monoxide and metallic lead

by the mode of preparation, its composition also varies with the temperature and time of heating Although there is little doubt that a compound of the empirical formula Pb_3O_4 does exist, most red leads of commerce appear to contain Pb_3O_4 with variable amounts of lead monoxide Conversely, litharge generally contains a little red lead Many varieties of red lead approximate in composition to Pb_4O_5, and these red leads no doubt contain $Pb_3O_4 + n PbO$ As with lead sesquioxide, dilute acids decompose Pb_3O_4 into PbO and PbO_2, the former dissolves in the acid forming a salt of lead When heated, red lead dissociates into lead monoxide and oxygen $2Pb_3O_4 \rightleftharpoons 6PbO + O_2$ The dissociation pressure varies with the temperature, thus

Temperature	445°	500°	555°	636°
Pressure .	5	60	183	763 mm

The partial pressure of oxygen in air is one fifth of 760 mm, that is, 152 mm This means that red lead will decompose at about 550° when heated in air, and in pure oxygen at atmospheric pressure, red lead can be formed at 600°, but not at 650° Red lead proper is not a mixture of lead monoxide and lead peroxide because the dissociation pressure of lead peroxide at a given temperature is much less than that of red lead Red lead is used in the manufacture of flint glass and glazes for pottery It also is used in the manufacture of paint and of matches

§ 8 Lead Peroxide

Lead peroxide is prepared by the action of oxidizing agents—hypochlorites, chlorine, bromine, hydrogen peroxide, or persulphates—on alkaline solutions in which lead monoxide is suspended The same compound is deposited on the anode when a solution of a lead salt is electrolyzed Lead peroxide is a strong oxidizing agent Thus, when lead peroxide is gently rubbed with sulphur on a warm surface the mass inflames, with phosphorus, the mixture detonates, when sulphur dioxide is passed over lead dioxide, the two unite to form lead sulphate, $PbSO_4$, and when hydrogen sulphide is allowed to impinge on a few grams of lead peroxide, the gas is oxidized and bursts into flame

Lead dioxide dissolves in a boiling concentrated aqueous solution of potassium hydroxide, and the solution on cooling deposits crystals of potassium metaplumbate, $K_2PbO_3 \, 3H_2O$, analogous with potassium stannate, $K_2SnO_3 \, 3H_2O$ If a mixture of calcium carbonate and lead monoxide be heated to 700°, carbon dioxide is given off and oxygen is absorbed forming calcium metaplumbate, $CaPbO_3$ If calcium plumbate be treated with carbon dioxide at the same temperature the reaction is reversed, and oxygen is evolved. This process was proposed by Kassner for the preparation of oxygen Hence lead dioxide shows feeble acidic properties Lead in lead dioxide is undoubtedly quadrivalent, as lead is in lead tetrachloride and lead fluoride—$PbCl_4$ and PbF_4 Lead dioxide behaves as a feeble base with acetic acid When red lead is dissolved in glacial acetic acid, pale green needle like crystals of lead tetracetate separate from the solution. The salt is immediately decomposed by water and brown lead peroxide is precipitated

The constitution of the higher oxides of lead —Lead peroxide is a

polyoxide $O{=}Pb{=}O$ because it gives oxygen, not hydrogen peroxide, when treated with acids Thus with concentrated sulphuric acid $2PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O + O_2$, and with concentrated hydrochloric acid, it gives chlorine $PbO_2 + 4HCl \rightarrow 2H_2O + PbCl_2 + Cl_2$ Lead peroxide is best regarded as the anhydride of orthoplumbic acid, $Pb(OH)_4$ or metaplumbic acid, $PbO(OH)_2$, just as CO_2, SiO_2, SnO_2 and MnO_2 are the anhydrides of carbonic, silicic, stannic, and manganous acids When hypochlorites, or other oxidizing agents, act upon an alkaline solution of lead monoxide, a brown precipitate of metaplumbic acid is formed $Pb(OH)_2 + 2NaOH + Cl_2 \rightarrow H_2O + 2NaCl + PbO(OH)_2$ If the latter be warmed, it passes into the anhydride PbO_2 The other two oxides of lead—Pb_2O_3 and Pb_3O_4—are in all probability salts of plumbic acid, lead sesquioxide appears to be lead metaplumbate, $PbPbO_3$, and red lead to be a lead orthoplumbate, Pb_2PbO_4

$\begin{matrix}HO\\HO\end{matrix}{>}Pb{<}\begin{matrix}OH\\OH\end{matrix}$	$Pb{<}\begin{matrix}O\\O\end{matrix}{>}Pb{<}\begin{matrix}O\\O\end{matrix}{>}Pb$	$\begin{matrix}HO\\HO\end{matrix}{>}Pb{=}O$	$Pb{<}\begin{matrix}O\\O\end{matrix}{>}Pb{=}O$
Orthoplumbic acid, H_4PbO_4	Lead orthoplumbate, Pb_2PbO_4, *i e*, Pb_3O_4	Metaplumbic acid, H_2PbO_3	Lead metaplumbate, $PbPbO_3$, *i e*, Pb_2O_3

Calcium orthoplumbate, Ca_2PbO_4, is a crystalline salt analogous with red lead, that is, lead orthoplumbate, and potassium metaplumbate, K_2PbO_3, is analogous with lead sesquioxide, that is, with lead metaplumbate

When lead sesquioxide is treated with nitric acid, it forms brown plumbic acid, $PbO(OH)_2$, or its anhydride, PbO_2

$$O{=}Pb{<}\begin{matrix}O\\O\end{matrix}{>}Pb + 2HNO_3 \rightarrow O{=}Pb{<}\begin{matrix}OH\\OH\end{matrix} + Pb(NO_3)_2$$

analogous with the action of nitric acid on lead carbonate

$$O{=}C{<}\begin{matrix}O\\O\end{matrix}{>}Pb + 2HNO_3 \rightarrow O{=}C{<}\begin{matrix}OH\\OH\end{matrix} + Pb(NO_3)_2$$

Similarly, with red lead

$$Pb{<}\begin{matrix}O\\O\end{matrix}{>}Pb{<}\begin{matrix}O\\O\end{matrix}{>}Pb + 4HNO_3 \rightarrow O{=}Pb{<}\begin{matrix}OH\\OH\end{matrix} + H_2O + 2Pb(NO_3)_2$$

§ 9 Accumulators or Storage Cells.

If two corrugated lead plates be covered with a paste of litharge, PbO, and dipped in a 20 per cent solution of sulphuric acid, the litharge on the plates is converted into lead sulphate, $PbSO_4$ If an electric current be passed through the cell, hydrogen is evolved at the cathode, and oxygen at the anode during the electrolysis of the sulphuric acid The hydrogen at the cathode reduces the lead sulphate producing a grey film of "spongy" metallic lead $PbSO_4 + H_2 = H_2SO_4 + Pb$, and the oxygen at the anode transforms the lead sulphate into lead persulphate $2PbSO_4 + 2H_2SO_4 + O_2 = 2Pb(SO_4)_2 + 2H_2O$, and the persulphate is at once hydrolyzed into lead peroxide and sulphuric acid $Pb(SO_4)_2 + 2H_2O = PbO_2 + 2H_2SO_4$, with the result that a dark brown film of lead peroxide is formed on the lead plate The current may then be stopped

If the terminals of the cell be then connected with a suitable

resistance, a current of nearly two volts can be obtained, and this continues for about twelve hours. The cell is then said to be "discharged." The brown film of lead peroxide on the anode gradually disappears during the discharge of the cell, and a white film of lead sulphate takes its place. The reaction on the anode during the discharge of the cell is $PbO_2 + Pb + 2H_2SO_4 = 2PbSO_4 + 2H_2O$. When the cell is being charged, the reaction can be represented by the same equation taken from right to left

$$\underset{\text{Charge} \rightarrow}{2PbSO_4 + 2H_2O} \rightleftharpoons \underset{\leftarrow \text{Discharge}}{Pb + PbO_2 + 2H_2SO_4}$$

As soon as the peroxide has disappeared, the electromotive force of the cell drops rapidly, although the voltage keeps remarkably constant as long as any peroxide remains on the plate. This is illustrated by the curve, Fig. 304. The curve from *B* to *C* shows that the voltage remains nearly constant for ten to twelve hours while the cell is discharging; the curve from *C* to *D* represents the drop in voltage when the peroxide is almost all gone. The cell should be recharged before it has reached this condition, otherwise the efficiency of the plates may be reduced. Reversible cells of this kind are called "accumulators," "secondary cells," or "storage cells." An accumulator is thus a cell with metallic lead plates, and the plates specially designed to hold as large an amount of litharge or lead oxide as possible. The plates dip in dilute sulphuric acid. When charged the accumulator acts as if it were a cell $PbO_2 | H_2SO_4aq | Pb$. To summarize the changes at the electrode during charge and discharge

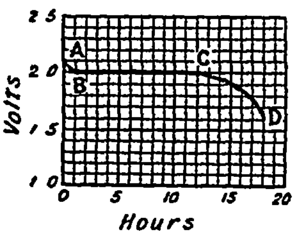


FIG. 304.—Voltage Drop of Accumulator.

	Charging	Discharging
Cathode	$PbSO_4 \rightarrow Pb$	$Pb \rightarrow PbSO_4$
Anode	$PbSO_4 \rightarrow PbO_2$	$PbO_2 \rightarrow PbO \rightarrow PbSO_4$

During the discharge, the surface of both plates becomes covered with a film of white lead sulphate, and hydrogen is evolved at the cathode: $Pb + H_2SO_4 = PbSO_4 + H_2$. The hydrogen is partly absorbed by the lead which has not been converted into sulphate. The presence of the absorbed gas raises the electromotive force of the cell during discharge until it is all consumed. This occupies but a few minutes; during this time, the voltage is represented by the curve *AB*.

Several other interpretations of the action in an accumulator during charge and discharge have been proposed. The hypothesis indicated above can be easily translated into the language of the ionic hypothesis. In the charged cell, we have a liquid containing H and SO_4'' ions, with lead and lead peroxide electrodes. When the cell is discharging, the H ions travel towards the PbO_2 plate and reduce the lead peroxide to lead monoxide: $2H + PbO_2 = H_2O + PbO$, and this plate accordingly receives a positive charge, owing to the de-electrification of the H ions. The SO_4'' ions simultaneously travel to the lead plates converting the lead at the surface of the plate into lead sulphate: $SO_4'' + Pb \rightarrow PbSO_4$, and

the plates are at the same time charged negatively In consequence, a positive current of electricity travels from the "peroxide" plate to the "lead" plate outside the cell, and from the "lead" to the "peroxide" plate in the liquid A secondary reaction between the sulphuric acid and the lead monoxide of the "peroxide" plate leads to the formation of lead sulphate, and consequently the consumption of the sulphuric acid in the liquid in the cell is relatively large during discharge When the cell is to be re charged, the "peroxide" plate is connected with the positive pole of the dynamo, and the "lead" plate with the negative pole of the dynamo The H ions of the cell travel to the negatively charged plate, an *equivalent* number of SO_4'' ions pass into the solution and metallic lead remains on the plate The effect is to reduce the lead sulphate back to metallic lead The SO_4'' ions travel to the positively charged "peroxide" plate and form lead persulphate $2SO_4'' + 2PbSO_4 = 2Pb(SO_4)_2$ The lead persulphate is immediately hydrolyzed to lead peroxide as indicated above Sulphuric acid is thus regenerated, and the cell is brought back to its original condition

§ 10. The Relationships of the Carbon-Silicon-Tin Family

The elements carbon, silicon, germanium, tin, and lead have a close family relationship The physical properties, it will be seen, where known, vary with the atomic weight Thus

TABLE LIX —PROPERTIES OF THE CARBON-TIN FAMILY

	Carbon	Silicon	Germanium	Tin	Lead
Atomic weight	12	28 3	72 5	119	207 1
Specific gravity	2 3 to 3 5	2 35	5 47	5 8 to 7 3	11 4
Atomic volume	4 15	12 04	13 26	18 25	18 18
Melting point	—	1350°	958°	231°	326°
Boiling point	—	about 3000°	—	2200°	1500°

The gradual change in the physical properties with rise in atomic weight is very manifest The chemical properties have many interesting resemblances. They are all bi- and quadri-valent, and there is a marked transition from acidic to basic qualities with rise of atomic weight Carbon and silicon form hydrogen compounds These relationships are best worked out by comparing the properties of the halides, the monoxides and peroxides, allotropic forms of the elements, etc Like bismuth in the phosphorus family, lithium in the alkali family mercury in the zinc family, lead seems to link this family with some other family.

§ 11 Titanium, Zirconium, Cerium, and Thorium.

	Titanium, Ti	Zirconium, Zr	Cerium, Ce	Thorium, Th
Atomic weight	48 1	90·6	140 25	232 4

Titanium —Titanium was discovered in 1791 by W Gregor while investigating the magnetic sand (menachanite) found in Menachan

(Cornwall) He called this element "menachin" Three years later, M. H Klaproth found what he supposed to be a new earth in rutile He called the metal derived from the earth "titanium," and, in 1797, he showed that titanium was identical with the menachin of McGregor The term "titanium" was derived from "Titans," the fabled giants of ancient mythology J J Berzelius first isolated the metal—more or less impure—in 1825

Titanium does not occur in nature free, but combined, small quantities are exceedingly common Most sands, clays, granitic rocks contain a small proportion, say, about 0 5 per cent Titanium has been detected in many mineral waters, in many plants, the bones of animals, in the atmosphere of the sun (by the spectroscope), etc The chief minerals are *rutile*, TiO_2 (tetragonal, sp gr 4 3), and the trimorphic *brookite*, TiO_2 (orthorhombic, sp gr 4 0), and *anatase*, TiO_2 (tetragonal, sp gr 3 9), titanium also occurs in minerals *ilmenite* (titaniferous iron ore), $FeTiO_3$, *sphene* or *titanite*, or calcium titanium silicate, $CaTiSiO_5$, that is CaO TiO_2 SiO_2

We have just seen that titanic oxide, TiO_2, is trimorphous, and isotrimorphous with stannic oxide, p 792 Anatase crystals appear to separate when a solution containing titanic oxide is at a temperature about 860°, at about 1000°, crystals of brookite, and rutile at higher temperatures. Titanic oxide, or titanium dioxide, TiO_2, is both acidic and basic It forms titanates when fused with alkalies, *e.g* potassium titanate, K_2TiO_3, when fused with potassium hydroxide It also forms salts, $TiCl_4$, $Ti(SO_4)_2$, etc, where titanium is a tetrad Titanic hydroxide, $Ti(OH)_4$, is precipitated from its salts by the addition of alkaline hydroxide or ammonia. Metallic zinc or tin reduces acidified solutions of titanic oxide to violet coloured titanic chloride, $TiCl_3$, where titanium is a triad. The corresponding oxide is titanium sesquioxide, Ti_2O_3 The titanic salts are not reduced by hydrogen sulphide or sulphurous acid. Hydrogen peroxide produces an orange yellow coloration in the presence of titanic salts, and this test is used for the colorimetric determination of titanium in rocks, etc The intensity of the colour is proportional to the amount of titanium present Vanadium salts in a similar manner produce a brick red coloration The yellow colour with titanium is supposed to depend upon the formation of titanium trioxide, TiO_3, where titanium appears to be sexivalent A series of bivalent titanium salts are known The corresponding oxide is titanium monoxide, TiO The metal is made by reducing the dioxide mixed with carbon in an electric arc furnace, and also by Goldschmidt's process The metal melts at 1850°, and burns when heated in oxygen, forming titanium dioxide, and at 800°, in nitrogen, it forms titanium nitride, Ti_3N_4 Titanium is closely related with silicon

Ferro-titanium (an alloy of iron with, usually, 10 to 15 per cent. of titanium) is used in the purification of Bessemer's and the open-hearth steel Enough titanium is added to give a steel containing 0 05 to 0 2 per cent. of titanium The addition also improves the durability and toughness of the metal Titanium carbide has been used as the negative pole for arc lighting, the positive pole being a rod of copper, or carbon One of the electrodes in the so called "magnetite" arc lamp is a mixture of magnetite and chromite with 15 to 20 per cent of rutile

Zirconium —While M H Klaproth was analyzing the mineral zircon, in 1788, he found one variety contained

Silica	Nickel and iron oxides	New earth	
31 5	0 5	68 0	per cent

Unlike aluminium, the new earth did not dissolve in alkalies The fact that the new earth was separated from zircon led to the term "*zirconia*," and "*zirconium*" *for* the corresponding metal, which was isolated by J J Berzelius in 1824 Several chemists have reported that zirconia is a mixture of two distinct earths one zirconia proper, and the other a new earth styled by L F Svanberg (1845), "noria," and by H C Sorby (1869), "jargonia" These pseudo discoveries have been traced to the contamination of zirconia with known elements—*e g* uranium, etc

Zircon is a silicate of zirconium, $ZrSiO_4$ Zirconium forms two series of oxides, ZrO_2 and Zr_2O_5 When zircon is fused with sodium carbonate, and the fused mass is treated with water, sodium zirconate, Na_4ZrO_4, and sodium silicate, Na_4SiO_4, pass into solution, the sodium zirconate is immediately hydrolyzed into insoluble zirconium hydroxide, $Zr(OH)_4$ This latter, on ignition, furnishes zirconium dioxide or zirconia, ZrO_2, which has both acidic and basic properties The metal is made by reducing the dioxide with carbon in the electric furnace Zirconia is used in place of lime in Drummond's lamp—zircon lamp Zirconia mixed with magnesia, thoria, etc, is used as filament in Nernst's lamp The mixture melts about 2200° Zirconia is also used in the manufacture of incandescent mantles, and in the preparation of very refractory crucibles, etc

Cerium —In 1803, M H. Klaproth discovered a new light-brown earth while analyzing a mineral from Ridderhyttan (Sweden) Klaproth called the earth "ochroite," from the Greek ὤχρος (ochros), brownish-yellow At the same time, and independently of Klaproth, J J Berzelius and W Hisinger made the same discovery, and named the earth "ceria" in honour of the discovery of the planet Ceres by G Piazzi, in 1801 The term "ceria" has been retained The element was isolated by Mosander in 1826 Ceria is one of the so called rare earths (*q v*), it occurs more particularly in cerite, euxenite, and monazite Cerium forms two oxides and two well-defined series of salts in which cerium is respectively ter- and quadri-valent Both oxides are basic The former furnishes white cerous salts—$Ce(NO_3)_3$, etc, the latter, orange-red ceric salts—$Ce(NO_3)_4$, etc.

Thorium —In 1818, J J Berzelius believed that he had discovered a new earth in a mineral from Fahlun (Sweden), and he gave it the name "thoria"—from Thor, son of the Scandinavian god Thor There was some doubt at the time about the novelty of this earth In 1828, Esmark discovered a mineral near Brevig (Norway) from which Berzelius isolated an earth very similar to that previously called "thoria." Esmark's mineral was subsequently called "thorite" The earth thoria was afterwards detected in many other minerals—thorianite (Ceylon), monazite, orangeite, orthite, euxenite, etc In 1862, J F Bahr thought that he had discovered a new element in a mineral resembling orthite This element was called "wasium" Bahr's wasium was afterwards identified with thorium Thorium is closely analogous in properties with zircon-

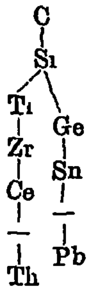
ium and silicon. Thoria is largely used in the manufacture of incandescent mantles (p. 755).

Family relationship of the group.—To summarize the physical properties of the related elements titanium, zirconium, cerium, and thorium:

TABLE LX.—PROPERTIES OF THE TITANIUM–THORIUM FAMILY

	Titanium	Zirconium	Cerium	Thorium
Atomic weight	48.1	90.6	140.25	232.42
Specific gravity	4.87	4.25	6.73	11.00
Atomic volume	9.88	21.32	19.92	21.13
Melting point	1795°	very high	830°	very high

The relationship of this group of elements to the carbon-lead family is sometimes represented by means of a diagram like that shown in the margin. The differences between cerium and thorium, and between tin and lead are supposed to indicate the existence of elements not yet discovered, and which are represented in the diagram by hyphens.



§ 12 The Rare Earths

> The rare earths form a group to themselves; chemically, they are so much alike that it taxes the utmost skill of the chemist to effect even a partial separation, and their history is so obscure that we do not yet know the number of them.—W. CROOKES.

In 1794, J. Gadolin discovered a new earth in the mineral gadolinite, which had been named in honour of himself; and in 1797 A. G. Ekeberg named the new earth yttria, after Ytterby, the place in Sweden where the mineral was found. C. G. Mosander (1843) noticed that what was then called yttria is really a complex earth containing yttria proper, and two other earths, which were oxides of two new elements, erbium and terbium. In 1880 P. T. Cleve found erbium earth not only contained erbium but also a new element thulium; and in 1886 Lecoq de Boisbaudran separated dysprosium from the same earth. In the same year, C. Marignac and Lecoq de Boisbaudran showed that terbium earth contained a new element gadolinium as well as terbium. In 1878, C. Marignac found the oxide of a new element in gadolinite. This he named ytterbium, after Ytterby (Sweden). In 1879, L. F. Nilson, while extracting ytterbia from the mineral euxenite, also separated an unknown earth which he called scandium, in honour of his country—Scandinavia—where the mineral was found. In 1839, C. G. Mosander separated the oxide of a new element from an earth which had hitherto been thought to be ceria. This earth he named *lanthanum*, λανθάνειν (lanthanein), to hide. In 1841, C. G. Mosander separated another earth—didymia—from lanthanum. The corresponding element was called didymium—from the Greek δίδυμος (didymos), hidden,

The rare earths include a curious group of basic oxides of elements which resemble one another so closely that they appear to form a series of compounds with properties which change but slightly from member to member The rare earths are found in the minerals mentioned under cerium, as well as in numerous other rare and scarce minerals. The rare earths are separated by first digesting the mineral with concentrated sulphuric acid. The clear filtrate is treated with hydrogen sulphide to remove copper, bismuth, etc The solution of the sulphates is treated with oxalic acid. The precipitate containing the oxalates of the rare earths is then separated into three main groups according to the solubility of their double salts with potassium sulphate Thus

Insoluble oxalates					
Insoluble double sulphates		Soluble double sulphates			
		Moderately soluble		Very soluble	
Scandium, Sc	44 1	Europium, Eu	152 0	Yttrium, Y	89 0
Lanthanum, La	139 0	Gadolinium, Gd	157 3	Dysprosium, Dy	162 5
Cerium, Ce	140 25	Terbium, Tb	159 2	Erbium, Er	167 7
Praseodymium, Pr	140 6			Thulium, Tm	168 5
Neodymium, Nd	144 3			Neoytterbium, Yb	172 0
Samarium, Sa	150 4				

Fractional precipitation.—It is very difficult to further separate the members of these series one from the other, and there is some uncertainty as to whether some so called elements are really homogeneous The elements of the rare earths are in many cases so closely related that they can only be separated into parts which give evidence of chemical individuality by very special and laborious methods The fractional separation of these elements depends on a reaction in which there is a difference in the behaviour of the elements, even though the difference be slight Suppose, for instance two earths differ slightly in basicity Add a weak solution of ammonia to a very dilute solution of the earths The dilution must be such that a turbidity appears only after the elapse of a considerable time The liquid is then filtered even while the precipitation is still incomplete There is now a slight difference in the basicity of the two portions of the earth so separated, for the portion still in solution is ever so slightly more basic than the portion precipitated by the ammonia The process is repeated on the two portions and the separated portions are again treated and the operations are so continued that the differences accumulate systematically and finally become perceptible by physical or chemical tests. The reaction most suitable for the fractional separation depends on the nature of the earths to be treated For example, fractional precipitation of the hydroxides by means of ammonia when the less soluble earths are deposited first, fractional crystallization of salts—bromates, oxalates, formates, etc

By fractional *precipitation*, Lecoq de Boisbaudran, in 1879, separated samarium from didymium (discovered by C G Mosander in 1841), and E Demarcay, in 1901, separated europium from samarium, the residual didymia was supposed to be the oxide of a distinct metal, didymium, with a definite atomic weight and which furnished salts whose aqueous solutions gave a characteristic absorption spectrum In 1885, by the fractional crystallization of a nitric acid solution of didymium ammonio-nitrate,

A. von Welsbach separated this salt into two other salts, one bright green and the other amethyst blue. The corresponding oxides were respectively pale green, and pale blue. The metal derived from the pale green oxide was called praseodymium—from the Greek πράσινος (prasinos) leek green, and the other was called neodymium—from the Greek νέος (neos), new. Aqueous solutions of the two fractions have distinct absorption spectra, but when mixed, in the right proportions, the original didymium spectrum is reproduced. The atomic weights of the two elements differ but slightly from one another—praseodymium, 140.6; neodymium, 144.3. This reminds us of the resemblance between cobalt 58.97, and nickel 58.68.

Meta-elements.—In 1887, W. Crookes argued very ingeniously that the closeness of the relationship between the metals of the rare earths makes it probable that these elements are modifications of one common element. For example, by a laborious process of fractionation, Crookes subdivided yttria into some eight components with different phosphorescent spectra, but the difference in the *chemical properties* of the fractions was so slight that, if it were not for a slight difference in the solubilities of the different fractions in ammonia, the fractions could not have been separated from one another. Crookes points out that the original yttrium passes muster as an element. It has a definite atomic weight, it enters into combination with other elements, and it can be separated from them as a whole. But the searching process of fractionation sorts the atoms of yttrium into groups with different phosphorescent spectra, and presumably different atomic weights, though from the usual chemical point of view all the groups behave alike. "Here, then, is a so called element whose spectrum does not emanate equally from all its atoms; but some atoms furnish some, other atoms others, of the lines and bands of the compound spectrum of the element. Hence the atoms of this element differ probably in weight, and certainly in the internal motions they undergo." Assuming that the principle is of general application to all the elements, and is limited by our knowledge of tests delicate enough to recognize the simpler constituent groups of the different elements, it is inferred that there are definite differences in the internal motions of the several groups of the atoms of a chemical element. The seven series of bands in the absorption spectrum of iodine, for instance, may prove not to emanate from every molecule, but "some of these molecules may emit some of the series, others others, and in the jumble of all these molecules, to which is given the name 'iodine vapour,' the whole seven series are contributors." Crookes thus introduced the conception of what he called **meta-elements** for those fractional parts of an element which resemble one another much more closely than one ordinary element resembles any other. The properties of the ordinary elements are supposed to be an average of the properties of aggregates of several meta-elements.

Questions.

1. Indicate the points of similarity and contrast between the dioxides of barium, lead and manganese.—*St. Andrews Univ.*

2. The molecular weight of litharge (an oxide of lead) is 223.1. The per cent. of lead is 92.8. The specific heat of lead is 0.031. Calculate the *exact* atomic weight of lead.—*Princeton Univ., U.S.A.*

3 Give the names and formulæ of the oxides of lead, and describe all that can be observed when each of these oxides is heated in an open crucible From 1 gram of one of the oxides of lead, 1 269 grams of lead sulphate can be obtained which of the oxides is it? ($Pb = 207$, $O = 16$)—*Sheffield Univ*

4 Starting with the metals tin and aluminium, show how you would make sodium stannate and sodium aluminate, and in what respect the two processes differ—*Amherst Coll., U S A*

5 What substances are formed when tin, iron, and zinc are severally dissolved in hydrochloric acid? Describe experiments to show that the solutions obtained from tin and iron are reducing agents, and explain why they differ in this respect from the zinc solution—*Sheffield Univ*

6 What would be produced if tin foil were introduced into solutions of the following salts, (1) silver nitrate, (2) lead acetate, (3) copper sulphate, (4) copper chloride, (5) stannous chloride, (6) alum, (7) ferric chloride? Give equations—*London Univ*

7 When iron stands in damp air it rusts When lead and silver are exposed to air they become tarnished Explain what has taken place in each case Do these changes cause any alteration in the weight of the metals?—*Aberdeen Univ*

8 Explain the modern processes adopted for the smelting of lead from galena, and in the desilverization and softening of the crude metal—*Board of Educ*

9 Enumerate the chief sources from which the following metals are obtained lead, tin, copper, and mercury Describe briefly the method by which any *one* of these is produced from its ores—*Aberdeen Univ*

10 Describe the extraction of lead from galena and of silver from argentiferous lead How may the oxides of lead be procured from metallic lead?—*St Andrews Univ*

11 When hydrogen is made in the ordinary way, to what is the disagreeable odour due? If tin were used instead of zinc, would you expect the same odour? (Explain from the method of purifying these metals)—*Amherst Coll, U S A.*

12 Explain how each of the following oxides can be prepared Barium dioxide, sodium peroxide, nickelic oxide, lead peroxide What is the action of hydrochloric acid on each of them, and by what chemical behaviour can they be classified into two groups?—*London Univ*

13 What is meant by the valency of an element? How is it determined? Is it always the same for the same element? If not, have any relationships been found amongst the valencies of an element? What are the valencies of nitrogen, carbon, lead, iron?—*London Univ*

14. To determine the equivalent of lead, Stas converted 103 grams of the pure metal into 164 775 grams of pure dry nitrate by evaporation with nitric acid Assuming the atomic weight of oxygen to be 16, and of nitrogen 14 04 calculate the equivalent of lead The specific heat of lead at 15° was found by Naccari to be 0 03 Calculate the atomic weight of lead and explain why a determination of the specific heats leads to a knowledge of the atomic weight—*London Univ*

15 Select any two substances out of the following list which could exist together in aqueous solution without any precipitation taking place—$Al_2(SO_4)_3$, $CuSO_4$, KNO_3, $ZnSO_4$, $NaCl$, $Pb(NO_3)_2$, $FeCl_3$, $(NH_4)_2CO_3$, $BaCl_2$, K_2S, $Ca(NO_3)_2$, NH_4Cl, $KClO_3$—*R Galloway*

16 Describe what occurs when hydrogen sulphide is passed (until there is no further action) into solutions of (*a*) caustic potash, (*b*) nitric acid, (*c*) stannic chloride, (*d*) ferric chloride, (*e*) chromic acid and sulphuric acid, (*f*) iodic acid, (*g*) sulphurous acid.—*Owens Coll.*

CHAPTER XLII

THE CLASSIFICATION OF THE ELEMENTS

§ 1 The Law of Octaves—J A R Newlands

> The primary object of classification is to arrange the facts so that we can acquire the greatest possible command over them with the least possible effort

THE classification of the elements has long been an attractive subject The elements have been classed into metals and non-metals, into acidic and basic, or, what amounts to the same thing, into electronegative and electropositive elements, they have been classed according to their valency, and also according to many other properties. In all these systems an element appeared in more than one class, or elements with but few properties in common were grouped together The properties of the elements used as the basis of classification may also vary with the conditions under which the properties are observed.

In all chemical changes one property at least remains unaltered, and the more successful systems of classification have been based on this property, the atomic weights of the elements The early efforts in this direction were seriously hampered by the uncertainty in the numerical values of the atomic weights. But after chemists had cleared up the confusion associated with the atomic theory left by Dalton, and obtained a consistent system of atomic weights, the results were more promising True enough between 1816 and 1829, J W Doberemer noticed some regularities in the atomic weights of certain related elements, for he found that most of the chemically related elements either exhibited almost the same atomic weight—*e.g* iron, cobalt, and nickel—or else exhibited a constant difference when arranged in sets of three Thus, selecting one set from Doberemer's list, and rounding off the modern atomic weights,

	Calcium		Strontium		Barium
Atomic Weight	40		87		137
Difference		47		50	

Many felt intuitively that the list of Doberemer's triads was but a fragment of a more general law Between 1863 and 1866, J A. R Newlands published a series of papers in which he arranged the elements in the ascending order of their atomic weights, and noticed that every succeeding eighth element was "a kind of repetition of the first" Thus,

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe

"In other words," said Newlands, "members of the same group of elements stand to each other in the same relation as the extremities of one or more octaves in music This peculiar relationship I propose to provisionally term the law of octaves" Newlands noticed that elements belonging to the same group "usually" appeared in the same column, and he declared that all the numerical relations which had been observed among the atomic weights "including the well-known triads, are merely arithmetical results flowing from the existence of the law of octaves"

The "law of octaves" did not attract much attention probably because faulty atomic weights seriously interfered with the arrangement[1] Similar remarks apply to some papers by A E B de Chancourtois in 1862, where it was proposed to classify the elements by their atomic weights Chancourtois arranged the elements in a spiral line according to their atomic weights, and stated *les proprietes des corps sont les proprietes des nombres* Chancourtois' ideas were so much entangled with extraneous verbiage, and the truth was so much obscured by useless and faulty speculations, that his work lay buried for nearly thirty years, and it was only resurrected after Mendeeleff's system had become famous

§ 2 The Periodic Law—D I Mendeléeff and L Meyer.

> The periodic series is a brilliant and adequate means of producing an easily surveyed system of facts which by gradually becoming complete will take the place of an assemblage of the known facts —E MACH

D I. Mendeléeff and L Meyer, quite independently and, so far as we can tell, quite in ignorance of Newland's and Chancourtois' work, obtained a far clearer vision of the "law of octaves" about 1869 Mendeléeff said "When I arranged the elements according to the magnitude of their atomic weights, beginning with the smallest, it became evident that there exists a kind of periodicity in their properties" Otherwise expressed, if the elements be arranged in the order of increasing atomic weights, their *properties* vary from member to member in a definite way, but return more or less nearly to the same value at fixed points in the series Mendeleeff continued "I designate by the name 'periodic law' the mutual relations between the properties of the elements and their atomic weights, these relations are applicable to all the elements, and have the nature of a periodic[2] function." Expressed more concisely, Mendeléeff's periodic law The properties of the elements are a periodic function of their atomic weights The early tables were very imperfect for the reasons stated above Mendeleeff's tables of the atomic weights were designed to tabulate the elements in such a way as to exhibit the greatest number of relationships The original tables were afterwards amended and modified owing to improved data and the discovery of new elements The symbols of the elements with their atomic weights have been arranged on a helix, on a spiral, and in numerous other ways Table LXI, not very

[1] When Mr Newlands read a paper on "The Law of Octaves" at a meeting of the London Chemical Society in 1866, Prof G C Foster said that any arrangement of the elements would present occasional coincidences, and inquired if Mr Newlands had ever examined the elements according to their initial letters Twenty one years later the Royal Society awarded Newlands the Davy Medal for his discovery

[2] A periodic function is one whose value repeats itself at regular intervals. The interval is called a "period"

TABLE XLI.—THE PERIODIC SERIES OF THE ELEMENTS

		Series	Group 0	Group I R_2O	Group II RO	Group III R_2O_3	Group IV RH_4 RO_2	Group V RH_3 R_2O_5	Group VI RH_2 RO_3	Group VII RH R_2O_7	Group VIII Transition elements RO_4
1		1		H 1 008							
2	Short Period	2	He 3 99	Li 6 94	Be 9 1	B 11 0	C 12 00	N 14 01	O 16 00	F 19 0	
3	Short Period	3	Ne 20 2	Na 23 00	Mg 24 32	Al 27 1	Si 28 3	P 31 04	S 32 07	Cl 35 46	
4	Long Period	4	A 39 88	K 39 1	Ca 40 07	Sc 44 1	Ti 48 1	V 51 0	Cr 52 0	Mn 54 93	Fe 55 84, Co 58 97, Ni 58 68
		5		63 57 Cu	65 37 Zn	69 9 Ga	72 5 Ge	74 96 As	79 2 Se	79 92 Br	
5	Long Period	6	Kr 82 92	Rb 85 45	Sr 87 63	Yt 89 0	Zr 90 6	Nb 93 5	Mo 96 0	—	Ru 101 7, Rh 102 9, Pd 106 7
		7		107 88 Ag	112 40 Cd	114 8 In	119 0 Sn	120 2 Sb	127 5 Te	126 92 I	
6	Long Period	8	Xe 130 2	Cs 132 81	Ba 137 37	La 139 0	Ce 140 25			—	— — —
		9		—	—	—	—	—	—	—	
7	Long Period	10	—	—	—		—	Ta 181 0	W 184 0	—	Os 190 9, Ir 193 1, Pt 195 2
		11		197 2 Au	200 6 Hg	204 0 Tl	207 10 Pb	208 0 Bi	—	—	
	? Long Period	12	Nt 222 5	—	Ra 226 4	—	Th 232 4	—	U 238 5	—	

different in style from one of Mendeleeff's first tables, is one of the simplest modes of arrangement, perhaps the best[1]

The nine vertical columns are usually styled groups, and the thirteen horizontal lines series or periods. We have already studied the properties of the elements and of their compounds from the point of view of this system of classification Our brief reviews of the families or groups will therefore suffice to emphasize the relationships of the members of any given group Each short period, it will be observed, contains eight elements, and each long period either contains nineteen elements of which three are the so-called transition elements, or else it has provision made for nineteen elements. Hyphens are inserted in the spaces where the corresponding element is unknown The elements in the first short series are sometimes called group elements or bridge elements, since they show a notable gradation of properties from one to the other, and serve as links or bridges between the different groups. The members of the next short period or series 3, are called typical elements because they have the typical properties and characteristics of the group and show a rather wide divergence from neighbouring groups. Each typical element of the different groups diverges into two sub-groups

The transitional elements —It will be noticed that there is a distinct difference between the members of the odd and the even series The alternate even series, say the fourth and sixth, resemble one another more closely than the successive members of the odd series, say the fifth and seventh The lower oxides of the last members of the even series resemble in many ways the first members of the odd series Thus the basic oxides of chromium and manganese are in many ways similar to the oxides of copper and zinc Again, there are marked differences between the last members of the odd series (halogens) and the first members of the next even series (alkali metals) Those elements which cannot be placed in short periods fall in better with the last members of the even series and the first members of the odd series. Thus, iron, cobalt, and nickel fall between manganese and copper both with respect to chemical properties and atomic weights

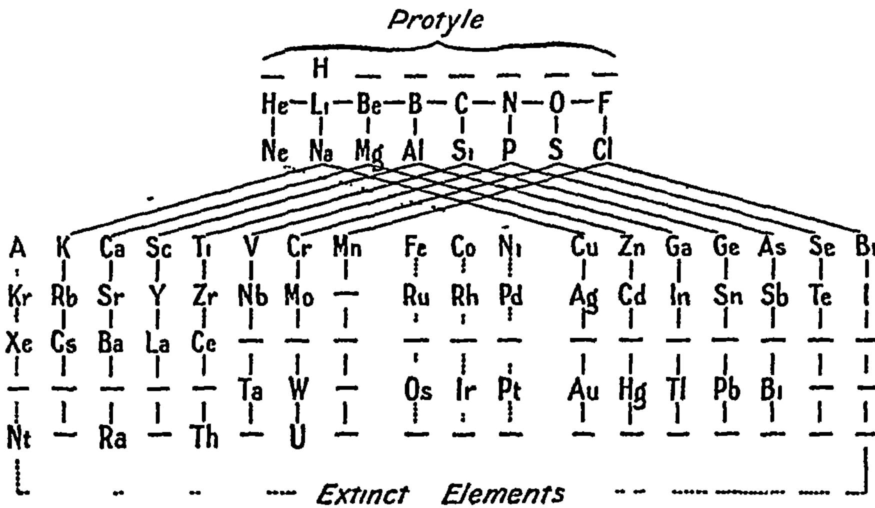
	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic weight	52	54 9	55 8	59 0	58 7	63 6	65 4
Specific gravity	6 9	7 4	7 8	8 7	8 8	8 9	6 9
Atomic volume .	7 5	7 4	7 1	6 8	6 7	7 1	9 5

so also Ru—Rh—Pd → Ag come just after the sixth series, and Os—Ir—Pt → Au after the tenth series. The inert gases are considered to form a kind of transition between the last members of the odd series (halogens) and the first members of the even series (alkali metals), and consequently also, they only occur in the horizontal rows where transitional elements in the eight groups are absent

The following arrangement, modified from one by T Bayley (1882), emphasizes the relationship and yet the individuality of the subgroups, the character of the transition elements, etc[2]

[1] Other schemes have advantages as well as disadvantages over Mendeléeff's arrangement so that there is no special reason why any one should be here given preference

[2] The meaning of "Protyle" and of "Extinct Elements" will be indicated in the discussion later on.



This table also emphasizes the fact that while the atomic weights of the elements progessively increase, their properties recur at definite intervals, no well known elements are omitted from the scheme, with three exceptions the order is that of the atomic weights, and the elements fall into virtually the same groups as would have been obtained had they been grouped according to their chemical behaviour

Most of the well defined physical and chemical properties of the elements are periodic—valency specific gravity, atomic volume, melting point, hardness, malleability, ductility, compressibility, coefficient of expansion, thermal conductivity, latent heat of fusion, refraction equivalents for light, colour, electrical conductivity, magnetic power, etc. When the numerical values of these properties and the atomic weights of the elements are tabulated on squared paper, a curve is obtained which is broken up into periods, as we have found to be the case in Fig 138 The properties of analogous compounds of the elements—molecular volumes, melting points, boiling points, stability of the hydroxides, colour, etc —are very often periodic The heats of formation of the chlorides, Fig 105, is a good illustration The specific heats of the elements are unique in furnishing a non periodic curve According to Dulong and Petit's law, if x denotes the specific heat of an element with an atomic weight, y, we have $xy = 6 4$ This is obviously a hyperbolic not a periodic curve like Fig 138

§ 3 The Gaps in Mendeleeff's Tables of the Elements

> The periodic law has given to chemistry that prophetic power long regarded as the peculiar dignity of its sister science, astronomy —H. C BOLTON

Both Meyer and Mendeleeff considered it necessary to leave gaps in their tables for undiscovered elements, and more particularly in order to keep certain related elements in the same vertical column Mendeleeff boldly prophesied that the missing elements would be discovered later, and in some cases even predicted their properties in considerable detail For instance, when Mendeléeff announced the law, there were

two blank spaces in group III., the missing elements were called eka aluminium and eka-boron respectively, and another space below titanium in group IV, the missing element in this case was called eka-silicon Th hypothetical character of these elements was considered to be an inherent weakness of the law, but the weakness was turned to strength when gallium scandium, and germanium subsequently appeared duly clothed with thos very properties which fitted closely with Mendeléeff's audacious prognostica tions This hit attracted considerable attention, and served to strengthen th faith of chemists in the fundamental truth of the periodic law In illustratio the case of eka-silicon and germanium is quoted side by side in Table LXI

TABLE LXII.—COMPARISON OF PREDICTED AND OBSERVED PROPERTIES OF GERMANIUM.

Eka silicon, Es (predicted in 1871)	Germanium, Ge (discovered in 1886)
Atomic weight, 72	Atomic weight, 72 3
Specific gravity, 5 5	Specific gravity, 5 47
Atomic volume, 13	Atomic volume, 13 2
Element will be dirty grey, and on calcination will give a white powder of EsO_2	The element is greyish-white and on ignition furnishes a white oxide GeO_2
Element will decompose steam with difficulty	The element does not decompose water
Acids will have a slight action, alkalies no pronounced action	The element is not attacked by hydrochloric acid, but it is attacked by aqua regia Solutions of KOH have no action, but the element is oxidized by fused KOH.
The action of sodium on EsO_2 or on EsK_2F_6 will give the element	Germanium is made by the reduction of GeO_2 with carbon, or of GeK_2F_6 with sodium
The oxide EsO_2 will be refractory and have a sp gr 4 7 The basic properties of the oxide will be less marked than TiO_2 and SnO_2, but greater than SiO_2	The oxide GeO_2 is refractory and has a sp gr 4 703 The basicity is very feeble
Eka-silicon will form a hydroxide soluble in acids, and the solutions will readily decompose forming a metahydrate	Acids do not precipitate the hydrate from dilute alkaline solutions, but from concentrated solutions, acids precipitate GeO_2 or a metahydrate
The chloride $EsCl_4$ will be a liquid with a boiling point under 100° and a sp gr of 1 9 at 0°	Germanium chloride, $GeCl_4$, boils at 86°, and has a sp gr at 18°, 1 887
The fluoride EsF_4 will not be gaseous	The fluoride $GeF_4\,3H_2O$ is a white solid mass
Eka-silicon will form a metallo-organic compound $Es(C_2H_5)_4$ boiling at 160°, and with a sp gr 0 96	Germanium forms $Ge(C_2H_5)_4$, which boils at 160°, and has a specific gravity slightly less than water

The confirmations of Mendeleeff's predictions of the properties of eka-aluminium (gallium), and of eka-boron (scandium) were equally striking. This dramatic achievement focused attention on the generalization, but it is only fair to say that the predictions and their subsequent verification are not such positive proofs of the truth of the periodic law as some suppose.

It is certainly wrong to say, as C Winkler did, "it would be impossible to imagine a more striking *proof* of the doctrine of periodicity of the elements than that afforded by this embodiment of the hitherto hypothetical eka-silicon," because gaps appeared in some of the older systems of classification, and the properties of the missing members could have been predicted, and the atomic weights estimated by analogy with the other members of the family, quite independently of, and in some cases better than, the periodic law.

§ 4 The Applications of the Periodic Law

> A natural law only acquires scientific importance when it yields practical results, that is, when it leads to logical conclusions which elucidate phenomena hitherto unexplained, when it directs occurrences till then unknown, and especially when it calls forth predictions which may be verified by experiment —D I MENDELÉEFF

Mendeleeff pointed out that the periodic law could be employed in 1 The classification of the elements, 2 The estimation of the atomic weights of elements not fully investigated, 3 The prediction of the properties of hitherto unknown elements, and 4 The correction of atomic weights.

1 **The classification of the elements** —T H Huxley (1864) has said "By the classification of any series of objects, is meant the actual or ideal arrangement together of those which are like, and the separation of those which are unlike, the purpose of this arrangement being to facilitate the operations of the mind in clearly conceiving and retaining in the memory the characters of the objects in question" The periodic system is undoubtedly superior to all the older methods of classification, for the law makes it possible to build up a system of the greatest possible completeness, free from much arbitrariness, and it furnishes strong circumstantial evidence of the correctness of the reasoning employed by Cannizzaro to deduce values for the atomic weights of the elements.

2 **The estimation of the atomic weights of the elements** —On account of practical difficulties, it is not always possible to fix the atomic weight of some elements by vapour density determinations (Avogadro's rule), and by specific heat determinations (Dulong and Petit's rule), and the atomic weights of these elements were frequently assigned on somewhat uncertain grounds According to C L Winkler, indium has the equivalent weight 37 8 The correct atomic weight must be some multiple of this, and for no special reason, the atomic weight was once taken to be $37\ 8 \times 2 = 75\ 6$ In that case, indium would fall between arsenic and selenium where it would be quite mis matched Mendeléeff proposed to make indium tervalent, like aluminium, so that the atomic weight became $37\ 8 \times 3 = 113\ 4$, and the element fell in the table between cadmium and tin where it fits very well The subsequent determination of the specific heat of indium, 0 0577, corroborated the change made by Mendeléeff in the atomic weight from 75 6 to 113 4. Beryllium, uranium, and a number of the rare earths at one time did not fit very well into the table, but Mendeleeff's alteration of the supposed atomic weights to make these elements fit the table were subsequently justified by vapour density determinations of the volatile chlorides, or by specific heat determinations

3 The prediction of the properties of hitherto undiscovered elements —In order to avoid introducing new names when speaking of unknown elements, Mendeléeff designated them by prefixing a Sanscrit numeral—eka (one), dwi (two), tri (three), etc —to the names of the next lower analogous elements of the odd or even numbered series of the same group Thus, the unknown elements of group I will be called eka-cæsium, and dwi-cæsium Were strontium unknown, it would be called eka-calcium In addition to the prediction of germanium, gallium, and scandium already discussed, Mendeleeff foretold the possible discovery of eka- and dwi-cæsium, eka-niobium—En = 146, of eka-tantalum—Et = 235, of dwi-tellurium—Dt = 212, and of the analogues of manganese eka manganese—Em = 100, and tri-manganese—Tm = 190

The case of the so called inert gases is of more recent date The discovery of argon and helium could not have been predicted from Mendeléeff's periodic law, but after these elements had been discovered, accommodated in the periodic table between the strongly acid halogen family and the strongly basic alkali metals, the probable existence of other similar inert gases was indicated. When an exhaustive search was made krypton, neon, and xenon were discovered with properties and atomic weights which could have been predicted from the arrangement made for argon and helium in Mendeleeff's table

4 The correction of the values of atomic weights —If the atomic weight of an element does not fit with the regular course of, say, the atomic volume curve, Fig 138, the atomic weight is probably in error Thus, the atomic weights of platinum, iridium, and osmium at that time were probably too high, and subsequent determinations verified this inference Thus the atomic weights of these elements were

	Platinum	Iridium	Osmium
In 1870	196 7	196 7	198 6
In 1912	195 2	193 1	190 9

There are also some misfits in the table as we have it to day, owing to the fact that at least three pairs of elements would be mis-matched if they were simply classed according to their atomic weights argon (39 88) and potassium (39 10), cobalt (58 97) and nickel (58 68), and tellurium (127 5) and iodine (126 92) The case of iodine and tellurium has been studied very closely Iodine most certainly belongs to the same group as the other halogens, and tellurium to the selenium group and these elements are accordingly placed in these groups in spite of the fact that if their atomic weights were alone considered tellurium would be ranked with the halogens, and iodine with selenium B Brauner supposes that ordinary tellurium is a complex containing α- and β-tellurium, but tellurium has been melted, sublimed, oxidized, hydrogenized, phenylated, dissolved, crystallized, and precipitated, yet nothing but failure has followed all attempts to get an atomic weight lower than iodine Hence in spite of the fact that "the laws of nature admit of no exception" (p 82), faith in the law has led chemists to allocate these discordant elements according to their chemical properties and not according to their atomic weights This method must be dubbed "unscientific,"[1] but the

[1] Bode's law of astronomy successfully *predicted* the asteroids and allocated their proper place in the solar system, but the subsequent discovery of Neptune did not agree with Bode's law The "*law*" was accordingly abandoned and it is now regarded as a curiosity

circumstantial evidence justifies the procedure, in the expectation that a consistent system will ultimately grow from the truth and error engrafted into the "law" It is not very probable that the principle underlying the periodic law will be abandoned because it is founded on a vast assemblage of facts of different kinds, and because it seems to be plastic enough to fulfil subsequent requirements

§ 5 Some Defects in the Periodic Law

The allocation of hydrogen in the table, as already indicated, is difficult, because hydrogen seems to be without companions It is univalent, and thus falls either with the alkali metals (D I. Mendeléeff) or with the halogens (O Masson) Hydrogen is electropositive like the alkali metals, but it is certainly not now considered to be a metal It can be displaced by the halogens from the organic compounds, and it forms hydrides with some of the metals not at all unlike the halogen salts Thus the position of hydrogen has not been definitely settled. Indeed, *hydrogen appears to be a "rogue" element quite out of place in the general scheme* Some suppose that hydrogen is a member of a series of independent elements yet unknown, the supposed last member of the series is called "proto fluorine", so also the elements "proto beryllium" and "proto-boron" have been invented, the former with an atomic weight 1 33, and the latter, 2 All this, however, is mere speculation

There is a difficulty about the allocation of the rare earths Most of them could be distributed about the table according to their atomic weights, or they could be relegated to a class by themselves B Brauner, who has made a special study of the rare earths, considers that they should all be grouped together with cerium so that "Ce, 140 25" in the table stands for

Ce, 140·25; Pr, 140 6; Nd, 144 3, Sa, 150 4, Eu, 152, Gd, 157 3; Tb, 159 2, Dy, 162 5, Er, 167 7, Tm, 168 5, Yb, 172 0

This has been called the asteroid theory of the rare earths The properties of the rare earths, however, are not well enough known to give us much confidence in the various proposals which have been made for dealing with them, and consequently, Mendeléeff considered that the installation of these elements should be deferred The better known elements of the rare earths fit well enough into the table, thus, ytterbium—Yb, 172—fits into group III, series 10, etc

If the properties of the elements are dependent on their atomic weights the existence of two elements with different properties and approximately the same atomic weights should be impossible Hence the difficulty with elements like cobalt and nickel, ruthenium and rhodium, etc The peculiarities of these elements would never have been suspected from the periodic law

Some elements are allocated places in the table according to their atomic weights in opposition to their properties For instance, copper, silver, and gold fall into one group with the alkali metals. The trivalency of gold appears to be unconformable with the valency of its companions although in its present position the series $PtCl_4$, $AuCl_3$, $HgCl_2$, and $TlCl$ is suggestive Thallium is very like lead, but its sulphate and some other salts are quite different from lead salts At least three pairs of elements have been placed according to their properties irrespective of

their atomic weights, as indicated by the "misfits" mentioned in the preceding section

Some elements which appear to be chemically similar are separated in the table For example, copper and mercury; silver and thallium; barium and lead, etc The position of these elements in the table gives no hint of these characters Still, it might be argued that these elements exhibit many essential differences Thus the physical properties of mercury and copper, and the properties of the cupric and mercuric chlorides and sulphates show great contrasts. The stability of cuprous and mercurous chlorides is also very different Lead and barium peroxides appear to have a different constitution The unstable thallium sesquioxide, Tl_2O_3, corresponds with the other—more stable—sesquioxides in the group, but there are many important points of resemblance between thallium and the alkali metals, and between silver and lead

G Wyruboff (1896) has the idea that the periodic system is "a very interesting and highly ingenious table of the analogies and the dissimilarities of the simple bodies—a mere *catalogue raisonne* of the elements", and further, "since the laws of nature admit of no exception, the periodic law must be considered as a law of nature definitely established which must be accepted or rejected as a whole" Wyruboff's proposal to reject the periodic law is somewhat precipitate, for we do not feel quite satisfied that the supposed misfits are not due to defective knowledge There is a distinction between "failure" and "incomplete success"

§ 6 The Unitary Theory of Matter.

Chemistry marches towards its goal and towards its perfection by dividing, subdividing and subdividing still again.—A. L LAVOISIER, 1789

Simplicity is the seal of truth Nature is wonderfully simple, and the characteristic mark of a childlike simplicity is stamped upon all that is true and noble in nature —M SENDIVOGIUS (1650)

Belief in the simplicity of nature is not logic but faith pure and simple It is one of those insidious and dangerous *tacit* assumptions which often creep into scientific theories Tacit assumptions are "dangerous" because they are usually made unconsciously, so that they appear to be self-evident truths, and prevent our harbouring the shadow of a doubt of their insidious character True enough, as H Poincaré has said "Every generalization supposes in a certain measure a belief in the simplicity of nature every law is considered to be simple until the contrary has been proved," but faith in this dogma has sometimes led men astray In consequence, hypotheses have frequently flourished in spite of experimental evidence to the contrary It is not at all uncommon to find a "law" which appears to be quite simple, when the methods of measurement are crude and approximate, becomes exceedingly complex when more accurate data are available We have found this to be the case, for instance, with Boyle's law, Charles' law, etc Another example will now be given

There was a marked tendency among the earlier Greek philosophers to postulate one single kind of matter a πρώτη ὕλη—(prote) first, (yle) matter—or primal element This *prima materia* ("potential matter") was supposed to consist of parts which when grouped in different ways produced the various kinds of matter considered by them to be elemental

The hypothesis is sometimes called the unitary theory of matter all the different forms of matter in the universe are derived from one and the same primordial element.

The philosopher Anaximenes regarded air as the primal element Herakleitos, fire, Pherekides, earth, Prout, hydrogen, and modern chemical philosophers, electrons, and possibly æther Thales of Miletus, who flourished in the sixth century B C, considered that water was the first principle Thales' doctrine had many supporters—J B van Helmont (1682), etc —it lived for nearly twenty five centuries, and it was demolished in 1770 when Lavoisier demonstrated that water cannot be changed into earth (p 25)

In 1815 and 1816, W Prout tried to show that the atomic weights of the elements were exact multiples of the atomic weight of hydrogen, so that an atom of any element must weigh a certain number of times as much as an atom of hydrogen Hence added Prout, "we may almost consider the πρώτη ὕλη of the ancients to be realized in hydrogen" According to Prout's hypothesis, the elements are different aggregates of the atoms of primordial hydrogen, that is, the different elements are polymers of hydrogen, in consequence, within the limits of experimental error, the atomic weights of the different elements should be expressible by whole numbers when the atomic weight of hydrogen is unity

Many writers attracted by its apparent simplicity gave unqualified support to Prout's hypothesis, but an impartial review of the facts with very much more refined data than were available in Prout's day, led J S Stas (1860–1865) to state "I have arrived at the absolute conviction, the complete certainty, so far as is possible for a human being to attain to certainty in such matters, that the law of Prout is nothing but an illusion, a mere speculation definitely contradicted by experience" Many have tried to reconcile Prout's hypothesis with facts by changing the standard of reference to an imaginary primordial element with an atomic weight equivalent to half an atom of hydrogen (C Marignac, 1844), then to a quarter of an atom (J B Dumas, 1859) But having once begun to divide the hydrogen atom, there was no limit to the process of subdivision, and the hypothesis could then be made to fit any conceivable set of atomic weights This tinkering with Prout's hypothesis brought it, for a time, into disfavour

The elements, as we have seen, are substances which have never been resolved into simpler substances, we did not say that the elements could never be decomposed into a more primitive form (or forms) of matter **The atom of an element can be defined as a substance whose parts are held together by a force superior to any which has yet been brought to bear upon it** The elements have hitherto proved undecomposable, but it is quite conceivable that they are not absolutely undecomposable Much circumstantial evidence has accumulated in recent years which makes it increasingly difficult to believe that Dalton's atoms are absolutely indivisible, and to deny that all the different elements have been formed from one homogeneous simple primal form of matter which G Hinrichs has called pantogen (1857) W Crookes, protyle (1886), and J L G Meinecke, urstoff (1817) It has been said that protyle "is matter generalized, stripped of its distinctions, the same from whatever source derived, it is matter in potency rather than in

act, intangible, inaccessible to sense perception, probably indifferent to the solicitations of gravity"

The idea that all the different forms of matter represent different stages in the growing complexity of one single elemental form of matter, has haunted the human mind from the earliest times, and the belief that "unity is the law of God," or that *simplex veri sigillum*, has proved so peculiarly fascinating that a remarkable number of speculations have been spun about this theme These ingenious and subtle systems are admirable works of art, but they are outside the realm of science so long as the evidence on which they are founded remains intangible and vague In recent years still another hypothesis is claimed to have been woven with circumstantial evidence which is rather more substantial than the incomprehensible fictions of the metaphysicians, for it can be examined and tested by comparison with gross material facts It is supposed that the elements have been developed by the condensation of a primitive form of matter, and that the different elements, as W Crookes expresses it, have been evolved by a kind of struggle for existence where elements, not in harmony with their environment, have either disappeared—*extinct elements*—or have never existed, where elements—*asteroidal elements*—have come into being and survived only on a limited scale as is the case with the *rarer elements*, and where other elements predominate because the surrounding conditions have been favourable to their formation and preservation, *e g* the *common elements* This circumstantial evidence can now be outlined

1 Why do so many atomic weights approximate to whole numbers?—The International Table of Atomic Weights, 1916, contains 83 elements, and of these, 43 are integers within one-tenth of a unit This fact has nothing to do with Prout's discarded hypothesis, but the numbers are facts which can hardly be due to chance, because the probability of this occurring is exceedingly small—something like one in 20,000 millions It is argued that the approximation of the atomic weights of so many elements to whole numbers cannot be reasonably attributed to a fortuitous coincidence

2 Why do so many groups of the elements exhibit family relationships?—If the elements are totally distinct and independent of one another it is exceedingly difficult to reconcile the regularities and analogies of the elements in different groups revealed by a study of Mendeleeff's law, the main characteristic of which is *relationship* The periodic law dimly foreshadows an identical origin or common parentage of families of elements A study of the alkali metals, the metals of the alkaline earths, the halogens etc, makes it highly probable that the different elements of one family, at least, have been formed by the conglomeration of monads or atomicules formed of the same primal matter so as to build up ordinary atoms of different sizes or shapes, that the evolution has progressed from homogeneity to heterogeneity In other words, said C R A Wright (1873) the so-called elements are allotropic modifications of a primitive matter and they differ from one another in the amount of latent energy they contain per unit mass The idea is illustrated by the homologous series of carbon compounds For instance,

	Ethene C_2H_4	Propene C_3H_6	Butene C_4H_8	Pentene C_5H_{10}	Hexene C_6H_{12}
Molecular weight	28	42	56	70	84

apparently by the polymerization of an increasing number of CH_2 groups This series rises in a similar manner to nearly $C_{30}H_{60}$, with a regular increase of 14 in the molecular weight Doboreiner's triads too have emphasized similar "constant" differences in the atomic weights of related elements Hence, argued D Carnelley (1885), if a body we know to be compound can play the part of an element, there is some plausibility in the suggestion that the elements themselves are not absolutely simple

3 **Why are closely related elements so often associated together in nature?**—Chemists have long been struck with the peculiar way certain elements occur in the half mile crust of the earth Although no disturbing agent has been recognized at work in nature whereby the different kinds of elements are sorted like to like, yet certain groups of elements nearly always occur in juxtaposition These individual elements are not plentifully distributed, and they are not easy to separate from one another—*pares cum paribus facillime congregantur* For example, cobalt is perhaps never quite free from nickel, and *vice versâ*, silver is almost invariably associated with lead ores and with gold, cadmium with zinc ores, selenium with the sulphur of pyrites, the members of the two groups of the platinum elements, and the rare earths These associations and co mixings cannot be entirely due to chance, for these elements are neither plentifully distributed nor have they any marked chemical affinity for one another Consequently, it has been suggested that the elements in question were formed from some common material under almost identical conditions, and where slight variations in the conditions led to the almost simultaneous formation of closely related elements Environment has determined the path of the evolution of the elements

Additional circumstantial evidence for the unitary theory has been obtained from (4) the grouping of the spectral lines (p 819), (5) the magnetic perturbation of the spectral lines (p 821), (6) the phosphorescent spectra of the meta elements (p 804), (7) spectra of the stars and nebulæ (p 822), (8) electric discharges in attenuated gases (p 826), and (9) radioactivity (pp 834 *et seq*) This evidence will now be reviewed

§ 7 Evidence for the Unitary Theory from Spectrum Analysis

> The final impression our mind receives on contemplating these fundamental relations is that of a wonderful mechanism of nature, the functions of which are performed with never failing certainty, though the mind can only follow them with difficulty and with a humiliating sense of the incompleteness of its perception —J J BALMER

According to modern theories, elaborated in text-books on physics, light is produced by periodic vibrations of the æther, and light waves in the æther can be inaugurated by the motions of very small particles—atoms, or infra atoms—vibrating with a certain frequency [1] Each particle of matter vibrating with the right frequency can set up the periodic vibrations in the æther which we call light The eye only recognizes as light the vibrations of the æther ranging between the extreme red end of the visible spectrum (wave length 81 millionths cm), and the extreme violet

[1] It is not at all unlikely that the absorption of actinic energy by, say, insolated chlorine (p 239), is attended by a change in the vibratory motion of the atoms in the chlorine molecules, and that the vibratory energy is transmuted into an increase in the translatory motion of the molecules which causes the rise of temperature and other phenomena indicated on p 115

end (wave-length 36 millionths cm) The different vibrations are "sorted" by a glass prism (p 354) as spectral bands and lines or a complete spectrum Each particular band or line is an effect of the periodic vibrations of the particles The constancy of the spectral lines in the spectrum of a gas shows that the motions of the vibrating particles must be remarkably regular The period of vibration of the particles, as revealed by the spectroscope, conditions a chemical property which in the opinion of R Bunsen is as constant and fundamental as the atomic weight of the element, and which may be determined with almost astronomical exactitude, indeed, in 1900, the International Congress in Paris accepted a proposal by A de Gramont that no new substance be recognized as an element until its spark spectrum has been measured, and shown to be different from that of every other known form of matter. The large number of spectral lines in the spectra of many elements, *e g.* iron, shows that the vibrations which give rise to the spectrum must be remarkably complex According to J N Lockyer, the lines are connected with the different vibratory powers of different portions of an atom In other words, an atom is a complex aggregate of particles, and hence H A Rowland was led to say that a grand piano must be a simple mechanism in comparison with a vibrating atom All this is supposed to imply that the spectral lines are due to the vibrations of particles smaller than the atom, and that the atom itself is a complex system made up of vibrating corpuscles (*cf* p 804) Indeed, *the atom itself is now considered to be a kind of miniature planetary system embracing hundreds of corpuscles each spinning in its own tiny orbit* This recalls the speculation of p 121, where the individual atoms were supposed to whirl rhythmically in minute orbits to form molecules, much as the planets in the solar system revolve about the sun The idea is quite an old one S Brown, for example, in 1843, said

> The atom is by no means essentially or even potentially indivisible There is a possibility and likelihood that within the atom is another nameless world of the universe Under the sky of the atom proceed worlds of material existence as different from atoms as atoms from compound particles, as compound particles from crystal shapes, as crystal shapes from stars and planets, as stars and planets from solar systems, or as solar systems from firmaments

The homologous grouping of the spectral lines —At first glance, the spectral lines of a given element seem to be so complex that any attempt to reduce them to order appears to be hopeless The spectrum of iron, for instance, contains over 4000 lines G J Stoney (1870) noticed a semblance of order in the spectrum of hydrogen, and J J Balmer (1885) found that the wave lengths of most of these lines can be computed if whole numbers be substituted for m in a formula of the type $3647.2\,m^2/(m^2-4)$, and J S Ames (1890) showed that the error involved in the wave lengths of the 29 known hydrogen lines is accurate to about one part in 100,000 Thus,

		Hα	Hβ	Hγ	Hδ	Hε
	$m=$	3	4	5	6	7
Wave lengths	Calculated	6564 97	4862 93	4342 00	4103 11	3971 40
	Observed	6564 96	4862 93	4341 90	4103 10	3971 40

In the search for analogous laws in the spectra of other elements, it was found that the lines of many apparently chaotic spectra can be resolved into a number of regular series superposed one on the other Thus, the spectral

lines of the elements can be arranged in groups or series The spectrum of helium, for example, can be resolved into eight such series, each of which has lines which show a regular decrease in intensity with vibration frequency Oxygen has a spectrum with six superposed sets of lines, hydrogen and the alkali metals have each four such series The metals in question have monatomic molecules, and hence it inevitably follows that the atoms have a complex constitution, and that the spectral lines are not all produced by the vibrations of the same kind of particles, atoms are complex aggregates of vibrating corpuscles

Although the spectrum of each element is characteristic of that element and of no other, yet the spectrum of each of the five alkali metals can be resolved into four homologous series such that every line in one spectrum is represented by a corresponding line on all the other spectra, and generally, the spectra of related elements form natural or homologous groups The corresponding lines do not necessarily all occur in the visible spectra, e g the dark red line of the rubidium spectrum corresponds with a line in the ultra red in the other spectra, and the yellow lines of the sodium spectrum are homologous with lines in the ultra violet spectra of the other elements The spectra of related elements seem to be subject to a law of homology which is closely connected with their atomic weights Each series of homologous lines appears to contract in passing from one element to another so that as the atomic weight increases, the lines at the red end of the spectrum appear to open further apart, and at the violet end, to draw closer together Thus, by representing the spectral lines of the alkali metals by dots, Fig 305, so that their limits at the violet end coincide, it will be seen that the lines of this particular series contract in passing from lithium to cæsium, and the relation between the contractions and the atomic weights of the elements is shown in the diagram by making the distances between the lines represent the magnitude of their atomic weights

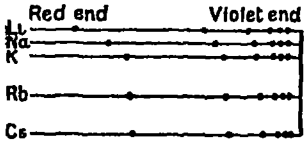


FIG 305 —One Series of Homologous Spectra of the Alkali Metals Spaced according to their Atomic Weights (C Runge, 1912)

There is thus a family likeness between the spectra of related elements, and a close connection has been traced between the atomic weights and the differences in the vibration frequencies of the lines in the members of a given family of elements The atomic weights of groups of related elements with their related physical and chemical properties differ by fixed definite values, and the spectra of these elements show that the masses of their atoms affect their rates of vibration in a similar manner This is taken to mean that not only is an atom of an element a complex composed of different aggregates of particles, but the atoms of allied elements are built up of similar aggregates of particles, and the observed differences in the spectra of allied elements results from differences in the way these aggregates are arranged in the atom

The atomic weights of certain elements have been calculated from the relationship of the spectral lines of allied elements For instance, the spectral lines of the magnesium calcium family can be grouped in three pairs, and the stronger lines of the radium spectrum are analogous with the stronger lines of the spectra of the other elements of the same family

The two lines of each of the three pairs are the same distance apart for any one element, but the distances apart of the lines in passing from one element to another increase in a regular manner with increasing atomic weights Thus

	Magnesium	Calcium	Strontium	Barium	Radium
Atomic weight	24 36	40 1	87 6	137 4	?
Distance	91 7	223	801	1691	4858 6 units

By plotting the atomic weights as functions of the distances between the lines, extrapolation furnished C Runge and J Precht (1903) an approximate value for the atomic weight of radium The extrapolation is easier if logarithms of the atomic weights and the distances apart of the lines be plotted The graph for a group of chemically related elements then lies in a straight line, as indicated in Fig 306 Lecoq de Boisbaudran (1886) evaluated the atomic weight of gallium and of germanium by a similar method

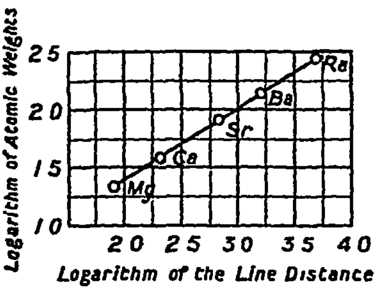


FIG 306 —Relation between the Atomic Weights and the Distance apart of the Spectral Lines of the Mg Ca Family of Elements.

The action of a magnetic field on the spectral lines—Zeeman's effect —P Zeeman (1897) found that the yellow line characteristic of the spectrum of sodium is displaced or "perturbed" because it is split into two separate and distinct lines And generally, the lines in the normal spectrum of an element are usually broadened into doublets, triplets, sextets, octets, or still more complex groups The effect will be evident from Fig 307 Different lines of the elementary spectra are perturbed

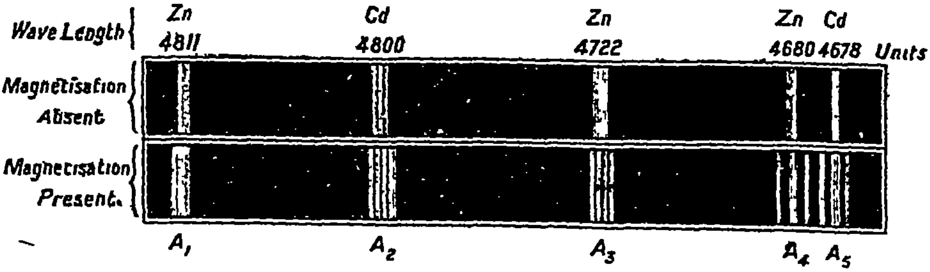


FIG 307 —Effect of Magnetic Field on the Spectral Lines of Zinc and Cadmium —Zeeman's effect

in different ways—some lines, originally single, may remain single, others give rise to doublets, triplets quartets, octets, etc There is a certain pathetic interest attaching to this phenomenon because it is said that the last experiment made by M Faraday (March 12, 1862) was an attempt to find if any spectral change could be detected when the source of the light is placed in a magnetic field Faraday's experiment failed because the only available magnet was not strong enough The perturbation of the spectral lines in a strong magnetic field is supposed to be due to alterations in the mode of vibrations of the sub-atomic particles under a magnetic stress The observed displacement depends on the

strength of the magnetic field If the spectrum be produced by the vibration of atoms of the same kind, it would be difficult to explain why the mode of vibration of atoms of the same kind can be altered in this way It is more reasonable to suppose that the different effects produced by a magnetic field on the different lines of the spectrum of a substance are due to the presence of different kinds of particles in the incandescent element This simply means that at the high temperature of the luminous object, the atoms of the element are dissociated into simpler "sub atoms" or corpuscles which are probably electrified when they are called electrons Owing to the fact that corresponding lines in the spectra of related elements—for instance, magnesium, zinc, cadmium—are similarly affected so that groups of lines in the different spectra undergo the same modification, it is inferred that the vibrating corpuscles which produce the A_1, A_2, A_3, lines in the spectrum of zinc are the same as the vibrating corpuscles which produce the A_1, A_2, A_3, lines in the spectrum of cadmium, etc Hence, not only is an atom a complex association of different corpuscles, but the atoms of allied elements probably contain certain groups of corpuscles, or sub atoms, in common "These observations," said T Preston (1899), "lend some support to the idea so long entertained merely as a speculation, that all the various kinds of matter, all the various so called elements, may be built up in some way of the same fundamental substance"

The spectra of stars and nebulæ—The nature of the spectrum of an incandescent body depends upon the temperature (p 356), and since the spectra of many elements have been observed at several different temperatures, it is possible to get a rough idea of the temperature of any incandescent element from the appearance of its spectrum For instance, the flame spectrum of sodium has two yellow lines close together, while the spark spectrum has a pair of lines in the orange and in the green, the flame spectrum of thallium has a single green line, and the spark spectrum has in addition some bands in the violet This fact is explained by the assumption that at the higher temperatures, the atoms of an element are aggregates of sub atoms, each of which has its own characteristic mode of vibration The spectra of the nebulæ, stars, and suns thus enable rough approximations of their temperature to be made

The sun, stars, and nebulæ, says A. M Clerke, form so many celestial laboratories where the nature and mutual relations of the chemical elements may be tried by more stringent tests than sublunary conditions afford In the very hottest stars[1] (estimated temperature 25,000°)—*e g* β Crucis—comparatively few chemical elements can be detected, while in the cooler red stars—*e g* Betelgeuse—the number of spectral lines is comparatively large and a large number of elements are present New elements appear to be introduced at each stage in the cooling of hot stars, so that elements which were non existent in the hotter stars make their appearance in the cooler stars, and a few elements disappear in passing from the hot to the

[1] In the orthodox works on astronomy, we are told that the nebulæ are the material out of which stars are made, and that in their forms, aggregations and condensations, the process of evolution of stars and suns can be traced The nebulæ begin either as hot attenuated gases or as clouds of cold meteoric stones which gradually gain heat as they clash together until finally they are converted into gases, and then gradually cool by radiation Hence the cooler stars are either young or old, heating up or cooling down. The hottest stars are in their prime,

cooler stars In the hotter stars little more than hydrogen can be detected, then follow hot stars with calcium, magnesium, and a few other elements superadded, then come cooler stars with more complex spectra corresponding with a greater variety of elements The planets, of which our own is a type, are among the cooler orbs If the different suns and stars be arranged in a series, the order of the appearance of the elements in the cooling stars is approximately the order of their increasing complexity as deduced from the magnitude of their atomic weights The lightest elements alone appear in the hotter stars These facts fit very well into the hypothesis that the matter of which stars are made, passes through a real change in the nature of the constituent elements, and that there is a progressive tendency of the elements to assume more stable forms in passing from the hotter to the cooler stars This corresponds with the assumption that the atoms are built of particles which form more and more complex aggregates as the temperature falls Carbon is an exception It has a low atomic weight, and yet it appears comparatively late, but the non-volatility of the solid element shows that the molecule is probably complex Calcium (atomic weight 40) appears before sodium (atomic weight 23), this may be due to the fact that the stability of the system of corpuscles which form an atom not only depends upon the number but also upon the mode of arrangement of the corpuscles In a general way, however, the elements appear in the cooling stars in the order of their increasing atomic weights The stars may thus be arranged in groups corresponding with different stages in their development The hydrogen and helium stars pass by insensible gradations into stars of the solar type, and finally into the deep red stars Thus, J N Lockyer (1887) states that

	Spectrum	Temperature	Appearance of the elements
Gaseous stars	Longest	Highest	Hydrogen, helium, asterium (a gas not known on earth)
Metallic stars	Medium	Medium	(a) Feeble spectrum of helium and hydrogen, magnesium, calcium, silicon and oxygen (b) No gases of the helium family, iron manganese, nickel, copper, etc.
Carbon stars	Shortest	Lowest	Carbon and compounds of carbon

Astronomers consider that the different stages in the evolution of sidereal systems cannot be demonstrated by the slow cooling of a *single* star, because the span of human life relative to the duration of cosmical events is far too short to enable the different stages to be followed in succession, these different stages can rather be followed by arranging the different nebulæ in a series so as to show all gradations, from a diffuse luminous haze to stars with faint nebulous halos The spectra of the gaseous and presumably younger nebulæ consist of three lines corresponding with hydrogen, helium, and some unknown elements—the great nebula in Orion is usually given as an example As the nebulæ grow older and more

compact, more lines corresponding with other elements appear These spectra are supposed to represent clusters of corpuscles more stable than the rest Hence, according to J N Lockyer's evolution hypothesis, the spectra of a properly arranged series of stars and nebulæ[1] indicate that the chemical atoms have grown during the cooling of the primal ultra-atomic gas much as visible rain drops grow from invisible water vapour Before hydrogen appeared, a whole series of lighter elements were probably formed by the gradual condensation (polymerization, etc) of the cooling "fire mist," and then passed into the heavier and more complex elements as the temperature fell still lower From a chemical point of view, therefore, the cooling of the primal matter has resulted in the formation of a succession of polymers $(1, 2, 3, \ldots)\eta$, where η is the density of the hypothetical protyle The polymerization may also proceed in successive stages $A = (1, 2, 3, \ldots)x$, $B = (1, 2, 3, \ldots)y$, $C = (1, 2, 3, \ldots)z$, where $x, y, z, \ldots$ represent the densities of simple forms of matter These complexes unite to form the series

$$An, Bm, Cp, \ldots$$
$$AB, BC, \ldots$$
$$ABC, \ldots$$

where $n, m, p, \ldots$ are integers The light elements—*asterium, coronium, nebulium*, etc —which appear to be present in some of the more attenuated nebulæ, and in the hotter stars, have probably long since vanished from the earth We infer their existence from their characteristic spectra Helium was once included in the list of light stellar elements unknown on earth (p 565)

Summary —The hypothesis which is supposed to correlate these and other facts may now be outlined Long before the earth was formed, it is supposed that a kind of ultra gaseous protyle was suffused throughout space, and, what has been called the "temperature" of the protyle, was inconceivably hotter than anything at present known on earth In course of time, some process, akin to "cooling," reduced the "temperature" of the protyle so that it was condensed into material atoms The simplest elements most nearly allied to the protyle would naturally condense first—thus, hydrogen and helium with their low atomic weights were born Then followed the elements next in order of complexity until finally uranium or radium was born We do not know an element with a greater atomic weight and presumably a more complex structure If the ideas developed in the next chapter approximate to the truth, even this element is not stable, and is slowly breaking down into simpler more stable forms As the temperature fell still lower, the earlier formed elements would unite among themselves and produce chemical compounds It is possible to reverse the process and dissociate chemical compounds by elevating the temperature (p 202), but it has not been possible to raise the temperature high enough to verify the hypothesis by "dissociating" the elements

[1] There is not much room for doubt about the theory with respect to the cooling of hot stars, but with nebulæ, S Arrhenius (1907) considers that great *cold* reigning in space has condensed all but the lighter elements into solid or liquid state, and these have gravitated to the interior The outer layer only is rendered luminous by dust particles and corpuscles flying into the nebula from space

Questions

1 Write an account of the general chemistry of silicon, having regard to its position in Group IV —*St Andrews Univ*

2 A new elementary body, a metal, is placed in your hands What means would you take to ascertain (1) its atomic weight, and (2) its position in Mendeleeff's table ?—*Science and Art Dept*

3 Show that the chemical properties of magnesium, zinc, and cadmium justify their position in the same group in the periodic classification —*Univ North Wales*

4 What was Prout's hypothesis ? Write an account of the history of the doctrine to the close of the investigations of Stas, including in it an account of his views —*Sheffield Univ*

5 It has been asserted that in all probability every well-defined property of an element is a periodic function of the atomic weight Explain precisely what is implied by this statement —*Science and Art Dept*

6 State the general characters of the magnesium zinc cadmium family of metals, and indicate their relations to the alkaline earths on the one hand and to aluminium on the other —*Science and Art Dept*

7 Reviewing the binary compounds, show that in the elements of the same family there is an increasing tendency as the atomic weight rises to form compounds having the electro negative element in larger proportion —*Owens Coll*

8 What grounds had Mendeléeff for predicting the existence of the elements gallium, scandium, and germanium ?—*Science and Art Dept*

9 Do you think the following a valid criticism of the periodic law, by M Berthelot (1885) ? Referring to the preceding question, " this prediction is not a consequence of the periodic series, it results purely and simply from the laws and analogies which have been known for many years, and which are independent of the new system "

10 Compare the properties (*a*) zinc and aluminium, *or* (*b*) manganese and iron, and their derivatives, and in the case of the pair selected explain why the two elements are placed in different groups in the periodic table —*London Univ*

11 Why is manganese included with chlorine in the same group of the periodic table ? With what elements besides the halogens is manganese related, and how is this relationship displayed ?—*London Univ*

12 Describe the general characters of the family of elements of which glucinium (beryllium) is the first term in the periodic scheme —*Board of Educ*

13 In the periodic scheme of the elements, lead appears in the same column as tin Justify this association by reference to the characters in which they agree —*Board of Educ*

14 Discuss the position of the helium family in the periodic classification —*St Andrews Univ*

CHAPTER XLIII

Radioactivity

§ 1 Electric Discharges in Attenuated Gases

A first step towards understanding the relations between æther and ponderable matter is to be made, it seems to me that the most hopeful foundation for it is knowledge derived from experiments on electricity in high vacuum —Lord Kelvin (1893)

The study of the phenomena attending the passage of electricity through gases has led to astounding developments during the past twenty years, and abundantly justified Lord Kelvin's prognostication Under ordinary conditions, gases are such poor conductors of electricity that they are classed as good insulators In order to get electricity to pass through air at ordinary atmospheric pressures, an electrical pressure approaching 30,000 volts per cm is required, and as the pressure of the air is diminished

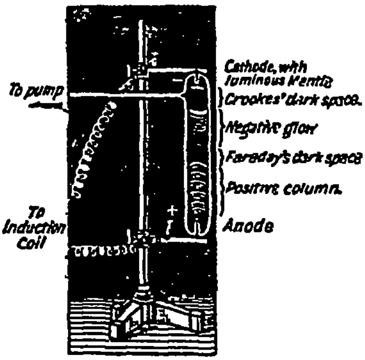


Fig 308

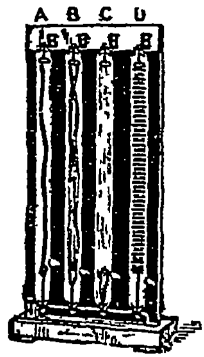


Fig 309

The Effect of an Electric Discharge on Attenuated Gases

the voltage required to produce a discharge diminishes in almost exactly the same proportion If a glass tube, about 30 cm long, Fig 308, be connected with a mercurial air pump, and the aluminium electrodes—disc and point—be connected with an ordinary induction coil and battery, either no spark, or thin zig zag sparks will pass through the tube, all depends on the distance of the electrodes apart, and on the electric pressure produced by the coil. If the pump be started, the spark passes more and more readily as exhaustion proceeds, first, forked brush-like bluish sparks begin to leap from electrode to electrode, when the pressure reaches 40 mm of mercury, a luminous red streamer appears as illustrated by the tube A, Fig 309, the red line widens, forming a fuzzy strip between the electrodes,

when the exhaustion is such that the pressure is about 10 mm, a luminous band fills the whole tube—*B*, Fig 309—and a violet halo surrounds the two electrodes At 6 mm pressure, the band begins to break up into layers—*C*, Fig 309—at 3 mm pressure, the tube appears to be filled with a number of transverse flickering reddish striæ, alternately light and dark [1], while the violet halos about the electrodes grow larger and larger—*D*, Fig 309—and a dark space—Faraday's dark space—appears at the negative electrode The prevailing colour of the pulsating striæ depends on the nature of the gas in the tube—with hydrogen the colour is red, and with chlorine green The aureole about the cathode separates from the flickering striæ and a dark space—Crookes' dark space—appears between the negative glow and the cathode, Fig 308 As exhaustion continues, the striæ diminish in number and size, and they appear to be paler in colour The light at the anode dwindles down to a luminous point, and Crookes' dark space at the cathode soon expands and finally fills the tube The glass then acquires a greenish-yellow phosphorescent light if the tube is made of soda glass. The pressure is then about 0·03 mm of mercury With further exhaustion the tube looks as if it were empty, but the glass still glows brightly, particularly about the cathode With still further exhaustions, the current from the induction coil is unable to pass through the vacuum tube The fact that the tube when highly evacuated is non conducting shows that *the electric current must somehow be carried from one electrode to the other by something*

§ 2 Cathode and Lenard Rays

The electron has conquered physics, and many worship the new idol rather blindly —H POINCARÉ (1907)

Whoever rejects faith in the reality of atoms and electrons, or the electro magnetic nature of light waves, or the identity of heat and motion, cannot be found guilty of a logical or empirical contradiction, but, he will find it difficult from his standpoint to advance physical knowledge —M PLANCK (1913)

W Hittorf (1869) showed that if a solid body—say a Maltese cross made of mica—be placed between the anode, *A*, and cathode, *C*, as in Fig 310, a true shadow appears on the glass, the shape of the cross shows that something must travel from the neighbourhood of the cathode in straight lines This "something" which causes the phosphorescence of glass was called by E Goldstein (1876) cathode rays Hence, (1) *the cathode rays travel in straight lines normal to the surface of the cathode, and they will cast a well-defined shadow if a solid object be placed between the cathode and the wall of the vacuum tube* The experiment can

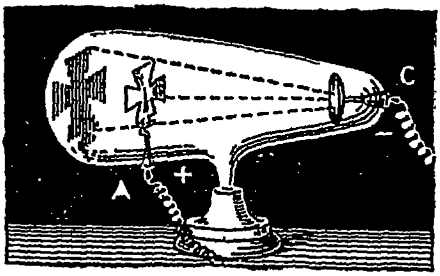


FIG 310 —Shadows Cast by Cathode Rays

[1] Glass tubes of about this degree of exhaustion—Geissler's tubes—are made in numerous patterns, and with different kinds of glass so as to get different fluorescent effects Tubes containing gases under reduced pressure and arranged for the passage of an electric discharge are called *vacuum tubes*

be varied in an ingenious manner, as shown by W Crookes (1879), Fig 311, by arranging the stream of cathode rays so that it strikes the upper vanes of a little paddle wheel which then rolls horizontally along a pair of parallel glass rails, away from the cathode By reversing the electric current, the wheel stops and then re volves in the opposite direc tion owing to the fact that the direction of the cathode stream has been reversed Hence, (2) *cathode rays can exert mechanical pressure.* By directing the cathode rays on to different minerals, beautiful phosphorescent effects may be obtained, Fig 312 Crystals of perthite, and didymium glass give a red phosphor escence, artificial rubies, and willemite a green phosphorescence, scheelite, yellow, Iceland spar, white, barium platinocyanide, zinc blende, etc, also glow and phosphoresce when exposed to the rays Hence, (3) *many minerals become phosphorescent when exposed to the cathode rays* The spectra of phos phorescent rare earths are of great value in studying these compounds The cathode stream, when focused on to platinum by means of a cathode shaped like a concave mirror, may heat the metal white hot, glass can be melted, diamonds charred, etc Hence, (4) *the cathode rays raise the temperature of bodies on which they fall* If the cathode stream be allowed to impinge on white rock salt or lithium chloride these salts are coloured violet The glass of the vacuum tube is also coloured after long use Hence, (5) *the cathode rays can produce chemical or physical changes*

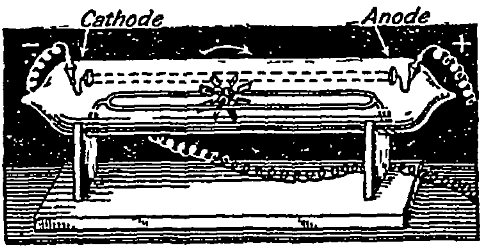


FIG 311 —Mechanical Motion by Cathode Rays

FIG 312 —The Effect of Cathode Rays on Minerals

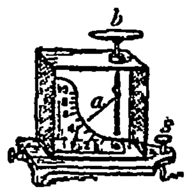


FIG 313 —Simple Electroscope

The Electroscope —The idea of the electro scope can be obtained from the simple form illustrated in Fig 313 *s* is a levelling screw, gold leaf *a* is fixed to a rod in metallic connection with a plate *b*, all insulated from the glass box There is a mica scale as shown in the diagram The method of working the electroscope is of course described in text books on physics If the electroscope be charged with positive or with negative electrification, the gold leaf *a* will diverge from the vertical rod as shown in the diagram. If an electrified body of opposite sign be brought in contact with the plate *b*, the leaf will descend a distance proportional to the magnitude of the charge, if the electrified body is charged sufficiently to neutralize the whole of the electrification of the electroscope, the leaf will com pletely collapse, and if the electrified body has a charge in excess of that of the electroscope, the leaf will collapse and then ascend charged with electricity opposite in sign to that previously held The height to which the leaf ascends is a rough measure of the magnitude of the charge Hence, if a substance capable of charging the ambient air electrically be placed on an insulated plate in the vicinity of a charged electroscope and the instrument be discharged, the rate at which the gold leaves converge will be proportional to the rate at which the air is electrically charged Much more refined instruments—electrometers—are employed in work

on radioactivity where it is estimated that one millionth of a millionth of a milligram of radium can be detected from its effect on the instrument, that is, a delicate electroscope is nearly a million times more sensitive than a spectroscope (p 356)

In 1895, J Perrin arranged a vacuum tube so that the cathode stream passed into a small metal cylinder inside the tube, and, by means of a wire, he connected the inner cylinder with an external electroscope The electroscope acquired a gradually increasing negative charge, or a positively charged electroscope was discharged Hence, (6) *the cathode rays are negatively electrified while the other contents of the tube are positively electrified* J Plucker (1858) showed (7) *the cathode rays can be deflected from their normal course by means of a magnet* This is illustrated by Fig 314, for if a magnet be directed to the side of the tube through which a discharge is passing, the focus of the rays can be deflected on to the walls of the tube The heat produced by the bombardment of the walls of the tube by the cathode stream will suffice to melt a little wax placed on the outside of the tube, *A*

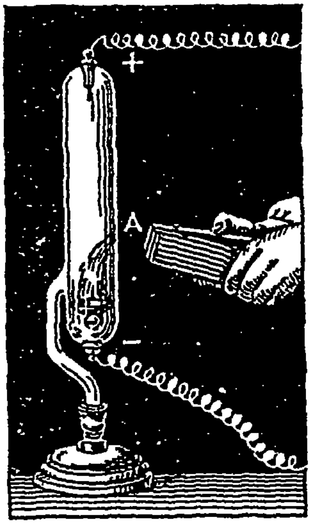


Fig 314 —The Effect of Magnet on Cathode Rays

P Lenard (1894) made a tube with a thin aluminium sheet—*D*, Fig 315—carried by a brass cap, at the end opposite the cathode *C*, a metal cylinder *A* served as anode Lenard found that the cathode rays passed through the aluminium window outside the tube, and were then called Lenard rays The cathode or Lenard rays are absorbed by different metals used as windows—the absorptive power of a substance is almost directly proportional to its density If the metal window is too thick, the cathode stream is arrested Hence, (8) *the cathode rays can penetrate and pass through thin sheets of metal, but not through thick sheets*

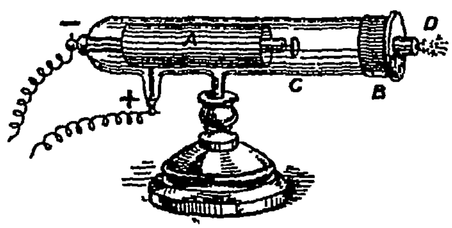


Fig 315 —Lenard's tube to bring the Cathode Rays outside the Vacuum Tube

At first, the cathode rays were thought to be a stream of negatively electrified atoms or molecules of the residual gas in the evacuated tube, C Varley (1871), or rather W Crookes (1879), suggested that they were particles or molecules of a fourth state of matter—an ultra-gaseous state which was called radiant matter—in which the free paths of the molecules were so long that collisions could be disregarded Owing to their high penetrative power (Lenard rays), and the fact that no difference in the properties of electrons can be detected by changing the kind of gas in the evacuated tube, nor by changing the electrodes, it follows that (9) *the cathode rays are independent of the kind of matter present, and if the particles be matter at all, the matter is the same in kind, from whatever source it is derived* E Wiechart (Jan , 1897) and J J Thomson (Apr , 1897) suggested

the startling hypothesis that what Crookes called "radiant matter" or the cathode rays, is a stream of negatively charged particles or corpuscles which have been formed by the disintegration of atoms of the gas in the vacuum tube The term electron was applied by G J Stoney (1881) to designate the unit or atomic charge of electricity, and it is now almost universally applied to the sub atomic particles supposed to stream from the negative electrode when a discharge is passing through an attenuated gas No difference can be detected in the corpuscles derived from different gases, and hence it is inferred that the electrons are common constituents of all gases If a stream of electrons be directed into an atmosphere of moist air, each electron serves as a nucleus about which moisture collects, and each electron becomes the centre of a visible drop of water Hence, (10) *a stream of electrons, when directed into moist air, forms a cloud* The cloud or mist is an aggregate of minute falling raindrops, and it is assumed that, like a particle of dust in moist air (p 168), an electron in moist air can serve as a nucleus for the condensation of the water vapour

The theory of the cathode rays —According to hypothesis, the electric discharge in attenuated gases splits the atoms of the gas into positively and negatively charged electrons The cathode rays are a stream of negatively charged electrons sent from the cathode with a high velocity It is inferred that ordinary atoms are probably made of nothing but aggregates of sub atomic particles—positively and negatively charged. Under ordinary conditions, the charges counteract one another and the atom is electrically neutral By the action of an electrical discharge, negative electrons are supposed to be detached from the atom, leaving a residue with a positive charge, and called a positive electron or positive ion If a negative electron attaches itself to a neutral atom, the latter will acquire a negative charge In reviewing the evidence derived from the properties of cathode rays J J Thomson (1897) said "The explanation which seems to me to account for the facts in the most simple and straightforward way is founded on the view of the constitution of the chemical elements which has been favourably entertained by many chemists" The view is that the atoms of the different chemical elements contain different aggregations of particles of the same kind, otherwise expressed, that a part at least of all atoms consists of electrons

Experiments which need not be detailed here have shown that in all probability the electric charge on an ion formed in the process of electrolysis, is the same as the electric charge of an electron, that the mass of an hydrogen ion is 1700 times the mass of an electron or negatively charged corpuscle, and therefore the mass of an electron is $\frac{1}{1700}$th the mass of a hydrogen atom—*i e* 7×10^{-28} grm, and its diameter is about 3×10^{-13} cm, whereas an atom of hydrogen has a mass of about $1\cdot3\times10^{-24}$ grm, and a molecule of hydrogen is about 2×10^{-8} cm, so that compared with the atom, the electron has quite a microscopic size The electrons can travel with a velocity ranging as much as 90,000 miles per second Their speed is dependent upon the intensity of the electrical force passing through the vacuum tube A cathode particle travelling at this speed could go nearly twice round the earth in a second The idea that the electrical condition of matter and its chemical activity depend upon the

addition or removal of electrons from atoms or molecules has been incorporated with the ionic hypothesis (p 307)

§ 3 Rontgen or X-rays.

We shall never succeed in exhausting unmeasurable nature —A VON HUMBOLDT

When the exhaustion of a vacuum tube is such that the tube is on the verge of becoming electrically non-conducting, and the glass opposite the cathode is brilliantly fluorescent, rays proceed from the fluorescent glass, *outside the tube*, these rays—called X-rays or Rontgen rays—have quite different properties from the cathode or Lenard rays, because they will pass through glass, and they are not deflected by a magnet Like rays of light, Rontgen rays can be reflected, refracted, and polarized, and they are not appreciably affected by the most powerful electric or magnetic fields as charged particles would be It is supposed that Rontgen rays—like the rays of light, radiant heat, and electro-magnetic waves—are due to pulses or waves set up in the æther by the impact of electrons on matter It is all a question of frequency or wave-length The following table gives the wave lengths of a number of radiations —

Radiation	Wave length in cm
Electromagnetic waves of wireless telegraphy	3×10^3 to 5×10^4
Longest heat waves known	6×10^{-3}
Infra red spectrum	6×10^{-3} to 7.5×10^{-5}
Red spectrum	6×10^{-5}
Green spectrum	5×10^{-5}
Violet spectrum	4×10^{-5}
Ultra-violet radiations	4×10^{-5} to 2×10^{-5}
Rontgen rays	10^{-8} to 10^{-9}

Hence, the wave length of the X-ray is about a thousand times smaller than the wave length of sodium light, and is comparable with the size of the atom In atmospheric air, the distance between neighbouring molecules is about 3×10^{-7} cm

The discoverer of the X-rays, W C Röntgen (1895), found that they can excite fluorescence on a paper screen coated with barium platinocyanide, $BaPtCy_4$, or calcium tungstate, $CaWO_4$, they can fog a photographic plate, and make the air through which they pass a conductor of electricity They have a remarkable power of penetrating substances opaque to ordinary light Rontgen rays are produced by the destruction of the cathode rays and are formed when the cathode rays impinge on solid objects Every substance when bombarded by electrons emits Rontgen rays—the glass walls of a vacuum tube, heavy metals like platinum or uranium, etc The penetrating power of Rontgen radiations refers to the decrease in the energy of a pencil of the rays which occurs when the rays are allowed to impinge on a solid Rontgen radiations with a low penetrative power, called *soft rays*, are emitted from a vacuum tube which has too much residual air The supply of electrons is then plentiful,

their speed is comparatively slow, and a current of comparatively low electromotive force is needed Conversely, radiations with a high penetrative power, called *hard rays*, are emitted if the tube be too highly exhausted The supply of electrons is then relatively small, their speed is comparatively high, and the necessary electromotive force is high

The rays emitted from an ordinary bulb are usually heterogeneous, mixed hard and soft, but C G Barkla (1906) showed that if the existing stimulus be great enough, every substance can be made to emit a set of X-rays which can be regarded as homogeneous and characteristic, in that the absorption coefficient, λ, of the radiations from that substance, in some standard substance (say aluminium), is a constant, *e.g*

	Ca	Cr	Cu	Se	Ag	Ba
λ	435 0,	136 0,	47 7,	18 9,	2 5,	0 8

Substances with atomic weights between aluminium and silver, emit two sets of these homogeneous characteristic radiations, *e.g* palladium emits two characteristic sets of homogeneous rays with wave-lengths respectively $0\ 58\times10^{-8}$ and $0\ 51\times10^{-8}$ cm, and nickel, $1{\cdot}66\times10^{-8}$ and $1\ 50\times10^{-8}$ cm respectively H G J Moseley (1913) further showed that when the increase in the atomic weight of the element is plotted with the corresponding decrease in wave-length, the curve does not run smoothly, but if the wave lengths or vibration frequencies be plotted against a series of natural numbers, the curve runs quite smoothly This is illustrated by Fig 316, in which the wave length $\times10^8$ cm is plotted against the numbers 13 to 30 ranging from aluminium to zinc for one of the homogeneous sets of rays Analogous curves have been obtained for all the known elements

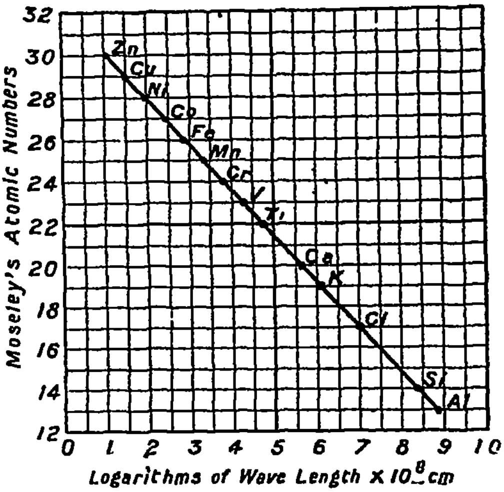


FIG 316 —Relation between the Wave length of the Characteristic X ray of the Elements and the Atomic Number

Indeed, the X ray spectrum of every element from aluminium to gold is determined by an integer *N* called the atomic number ranging from 13 for aluminium to 79 for gold There are some blanks corresponding with unknown elements The order of the atomic numbers is the same as the order of the atomic weights except where the latter disagrees with the order of the chemical properties so that the atomic number in the periodic table is a more fundamental index of quality than the atomic weight This shows that the wave-length, or the vibration frequency, of the characteristic X-rays from different elements changes from element to element by regular jumps The steady decrease in the wave length of the characteristic X-rays of a series of elements in the periodic table depends

on some fundamental property of the atoms As an hypothesis, it has been suggested that the increments are due to the successive addition of a unit electric charge to the nucleus of the atom, and that the magnitude of the nucleus of an atom is proportional to a number indicating the place of the element in the periodic table—hydrogen has a nucleus charge of one unit, helium two, etc

The atomic weights of the elements do not increase in an orderly way, they mount by steps of two, but not very regularly, and the elements sometimes appear to get in the wrong order, *e g* nickel comes *before* cobalt, but certain chemical properties and the wave-length of the characteristic X-rays from nickel show that it occupies a position *after* cobalt When the elements are arranged in this way the series shows gaps between aluminium and gold, presumably waiting to be filled by elements yet undiscovered

Action of X-rays on crystals —When a beam of ordinary light strikes a crystal, the latter behaves as if it were a continuous medium, because the structural units of the crystal are very small in comparison with the wave-length of the light, on the other hand, M Laue (1912) inferred that the wave-length of the X-rays is so small that the regularly arranged structural units of crystal will probably diffract the incident X-rays, much as a series of fine rulings on the surface of a metal plate diffract ordinary light This was soon verified by W Friedrich and P Knipping (1912) After a crystal has been exposed to a pencil of X-rays so arranged that the transmitted rays fall on a sensitive plate, photographs showing a series of symmetrically arranged dark spots—called Laue's spots—are obtained The different types of crystals furnish characteristic patterns, which are leading W H and W L Bragg to the discovery of some important facts on the internal structure of crystals

§ 4 Positive or Canal Rays

> The corpuscular theory of the positive rays has no other justification than that it explains our present day knowledge of the phenomenon in the simplest possible way —E GEHRCKE

When a perforated cathode is employed in the vacuum tube for producing cathode rays, E Goldstein (1866) first noticed that streams of

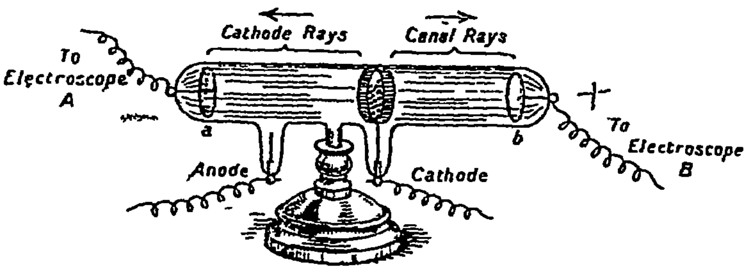


FIG 317 —Tube for Canal or Positive rays (After W Wien)

violet light passed through the perforations or canals and emerged behind the cathode on the side remote from the anode, and hence he called these streams *Kanalstrahlen* (canal rays) In the apparatus illustrated in Fig. 317, the canal rays travelling towards the right strike against a plate *b*

Intermediate stages of chemical action.—The photographic plate registers the rays within a millionth of a second after their formation, so that if a chemical reaction were taking place in the tube, it is possible that the method would disclose the existence of transient intermediate compounds as well as the final products of the reaction. For example, with *methane*, CH_4, five lines occur corresponding with particles having masses 12, 13, 14, 15, and 16. These must correspond with particles having the composition, C, CH, CH_2, CH_3, and CH_4. *Phosgene*, $COCl_2$, furnishes lines corresponding with particles having masses 99, 28 and 35.5, hence the decomposition proceeds by a separation of chlorine atoms from carbon monoxide without rupture of the carbon and oxygen atoms. No signs of a molecule NO_3 was observed during the oxidation of nitric oxide, NO, by oxygen.

Atomic weights.—The parabolic tracks recorded on the photographic plates enable the atomic weight of a gaseous substance to be determined within one per cent. of its true value without requiring more than 0.00001 gram of the substance. The result, moreover, is not dependent upon the purity of the material, for impurities merely produce additional lines in the positive ray spectrum, and do not affect the curves produced by the substance under examination.

New elements.—If a spectroscopist observed an unknown line in the spectrum of a discharge tube, he would infer the existence of an unknown substance provided the line were not produced by some alteration in the condition of the discharge; similarly, if a new curve be obtained in the positive ray spectrum, the probable existence of a new element would be inferred. Thus, atmospheric nitrogen gives a curve corresponding with a substance having an atomic weight 40 times that of a hydrogen atom, and is not indicated on the plate when chemically prepared nitrogen is employed. The positive ray method, too, is far more delicate than spectrum analysis, for it enables a foreign gas to be detected in quantities too minute to be revealed by the spectroscope. Thomson found unknown lines indicating that the gas which has been called neon is probably a mixture of two different gases of atomic weights 20 and 22—but with a preponderating amount of the former.

Allotropic hydrogen.—Thomson finds that the gas with atomic weight 3 is given off by most solids when bombarded by the cathode rays. It is interesting to remember that D. I. Mendeléeff (1871) predicted a new element of the halogen group with an atomic weight 3, but Thomson thinks that the gas in question is a triatomic molecule of hydrogen, H_3, mainly because (1) deliquescent salts or salts containing combined hydrogen—*e.g.* KOH, $CaCl_2$, LiOH—give continuous yields of the gas, while the supply with salts which do not contain combined hydrogen—*e.g.* LiI, Li_2CO_3, KCl—is soon exhausted. (2) Attempts to obtain spectroscope evidence of the new gas gave bright hydrogen lines with traces of mercury—derived from the apparatus used in manipulating the gas. (3) Vigorous sparking in the presence of oxygen, or contact with glowing copper oxide (or even exposure to bright light) destroys the gas. Assuming the gas is really H_3, it is more stable than ozone, more stable indeed than any known allotropic form of an element. If hydrogen is univalent, it is difficult to reconcile its existence with the ordinary views about valency. Thomson explains it by assuming that the hydrogen atom with its positive nucleus and negative corpuscles exerts a force analogous with that exerted by a magnet; and a group of

three atoms can arrange themselves about their axes to form a closed stable ring

§ 5 Becquerel Rays

The secret of all who make discoveries is to look upon nothing as impossible —J VON LIEBIG

About the time Rontgen (1895) discovered the peculiar X rays, radiating from phosphorescing Crookes' tubes, H Becquerel (1896) repeated some experiments of Niepce de St Victor (1867) in order to find "if the property of emitting very penetrative rays is intimately connected with phosphorescence" In other words, does the principle of reversibility (pp 25 and 202) apply? If Rontgen rays make a fluorescent substance shine in the dark, will a fluorescing substance emit invisible penetrative rays? Becquerel placed fragments of several phosphorescent substances on photographic plates wrapped in two sheets of black paper In about 24 hours, when the plates were developed, a silhouette of the phosphorescent substance appeared on the plate Hence, it was inferred that "*the phosphorescent salts of uranium must emit radiations which are capable of passing through black paper opaque to ordinary light, and of reducing the silver salts of the photographic plate*, even when the uranium compound has been completely sheltered from the light" The radiations emitted by the phosphorescent substance are called Becquerel rays, though Niepce, thirty years previously, noticed that uranium salts could affect photographic plates in the dark, and G le Bon (1896) called the radiations *lumière noire*—"black light" A substance which possesses the property of emitting these penetrative rays is said to be "radioactive," and the property itself is called radioactivity All substances containing uranium are radioactive The energy is not stored like light in a phosphorescent substance, because the property is no different whether insolated or non-insolated uranium be used, the energy does not come from the air because it is not affected by confining the uranium in a vacuum It is therefore probable that the uranium is slowly undergoing some spontaneous change as an effect of its internal energy Radioactivity does not depend upon light or heat, the emission of the rays appears to be a permanent and abiding property of uranium and its compounds, and it is independent of temperature and of all known physical conditions No sign of a diminution or increase of the property has been detected whether the substance be heated towards 2000° or cooled towards −200° The same weight of uranium, no matter how combined, emits the same amount of radiation. *The chemical properties of the elements—excepting perhaps the helium family—can be modified and controlled by changes in the chemical and physical conditions, but radioactivity is independent of these conditions* Consequently, the astounding assumption is made that radioactivity is an infra-atomic property, and is not the same type of phenomenon as an ordinary chemical reaction If chemistry be confined to the study of phenomena with the atom as unit, radioactivity regarded as an infra atomic phenomenon, is a kind of *meta chemistry*

Becquerel also found that when uranium is brought near to a charged gold leaf electroscope, Fig 313, the gold leaf gradually collapses The rate at which an electroscope is discharged is a measure of the efficiency

of the specimen in emitting rays The charged electroscope, indeed, is more sensitive than the photographic plate for detecting Becquerel rays Air which has been in contact with uranium and its compounds, like air which has been exposed to Rontgen rays, will discharge an electroscope, for exposure to these radiations makes air a conductor

G C Schmidt (1898) found that thorium is radioactive in the same sense that uranium is radioactive, and curiously enough, these two elements have the highest atomic weight—Th, 232, U 238 The radioactivity of thorium is readily shown by flattening an ordinary new gas mantle on the sensitive side of a photographic plate, and leaving all in darkness for about a week. When the plate is developed in the usual way, a photograph of the flattened mantle will be produced The mantle contains sufficient thorium, as oxide, to demonstrate the effect

It must be added that there are several strictly chemical reactions—hydration of quinine sulphate, action of sodium amalgam or calcium carbide on water, oxidation of phosphorus, combustion generally, *etc* —which have the power of rendering the ambient air a conductor of electricity so that it can discharge a charged electroscope, and an attempt has been made to find if the two phenomena are related. The temperature at which hydrogen and oxygen begin to combine in contact with carbon or platinum is almost the same, within the limits of the errors of measurement, as that at which these elements begin to form negatively charged electrons This, however, is not sufficient to justify a belief that there is a *causal nexus* between the two phenomena The property exhibited by many chemical reactions of making the ambient air electrically conducting must be sharply distinguished from radioactivity Ruthorford has emphasized the fact that the activity of radioactive bodies has these special characteristics (1) It is spontaneous, (2) It is exhibited by all the compounds of the radioactive elements, (3) It is not altered by changes in the physical or chemical condition of the element It might also be added that exposing metals to ultra-violet light, heating metal wires, splashing liquids, etc, also makes the ambient air electrically conducting

§ 6 Radium

It is the glory of God to conceal a thing, but the glory of a king to search it out —SOLOMON

For even the things which be in our hands—
These, knowing, we know not—so far from us,
In doubtful dimness, gleams the star of truth
ANON

Is the radioactivity of uranium due to the presence of an impurity?—P and S Curie tried to answer this question by examining the radioactivity of a number of uranium minerals They found the following relative results

	Units		Units
Pitchblende (Joachimstahl)	7 0	Uranium oxide (green)	1 8
Carnotite	6 2	Pitchblende (Cornish)	1 6
Chalcolite	5 2	Thorium oxide	0 1 to 1 4
Metallic uranium	2 3	Uranium nitrate	0 7
Orangite	2 0	Monazite	0 5

Obviously some uraniferous minerals are more active than uranium itself. Hence, it was inferred that "the strong activity of the pitchblende from Joachimstahl (Bohemia) is due to the presence of small quantities of a substance wonderfully radioactive, and different from uranium or any other simple body known." This result was confirmed by the extraction of the chloride of what was supposed to be a new element designated radium, Ra. The salt was over a million times more radioactive than uranium. One ton of pitchblende contains about 0.37 gram of radium, and about half of this is obtained by the following method of extraction.

The extraction of radium bromide or radium chloride from pitchblende.—The pitchblende is roasted with sodium carbonate and digested with dilute sulphuric acid; the solution contains uranium, and the residue contains radium and impurities. The residue is boiled with sodium hydroxide, washed with water, and then with dilute hydrochloric acid. The insoluble residue is digested with sodium carbonate to convert the sulphates to carbonates. Wash the insoluble carbonates with water, and dissolve the mass in hydrochloric acid. The solution contains radium, etc. Add sulphuric acid to precipitate the radium, etc., as sulphates. Again digest the precipitate with sodium carbonate, wash with water, and dissolve in hydrochloric acid. Hydrogen sulphide will precipitate radioactive polonium. The ton of pitchblende furnishes about 0.00004 grm. of this element. Oxidize the solution with chlorine and add ammonia, radioactive actinium is precipitated. The solution is boiled with sodium carbonate, washed with water, and evaporated to dryness with hydrobromic acid. On the addition of hydrobromic acid, radium and barium bromides are precipitated. These are separated by fractional crystallization.

The properties of radium and its salts.—The chemical reactions of radium chloride are so like barium chloride that a separation is very difficult, and a slight difference in solubility is the only means of separating the two. The bromides are more easily separated than the chlorides. The spectrum is characteristic and related to that of the alkaline earths. Metallic radium has been isolated by the electrolysis of radium chloride with an anode of iridiumized platinum and a mercury cathode. The radium amalgam so obtained was heated in a current of hydrogen to volatilize the mercury. A white metal remained. This melted at about 700°. The metal turns black in air, possibly owing to the formation of a nitride; it also chars paper; dissolves rapidly and completely in water and in dilute hydrochloric acid, thus showing that the oxide is soluble in the solvents named. 0.0919 gram of the anhydrous chloride, whose spectrum showed the presence of barium but faintly, gave 0.0859 gram of silver chloride. Hence, 0.0919 gram of radium chloride contains the equivalent of 0.0213 gram of chlorine; or 35.46 grams of chlorine unite with 117.5 grams of radium. Hence, the equivalent of radium is 117.5. If radium chloride be $RaCl_2$, by analogy with barium chloride, $BaCl_2$, the atomic weight of radium is nearly 235. Later determinations give rather lower values—226.5.

Radium appears to be a member of the family of alkaline earths. Its salts resemble the corresponding salts of barium. Radium sulphate is less soluble than the barium salt, the carbonate also is sparingly soluble. The

bromide and chloride crystallize with two molecules of water: $RaCl_2.2H_2O$, $RaBr_2.2H_2O$, and these crystals are isomorphous with the corresponding barium salts. The radium halides are much less soluble than the barium halides, and this enables radium to be separated from barium. Several other salts—nitrate, azoimide, cyanoplatinate, etc.—have been prepared. The radium salts when freshly prepared are white, but they afterwards become yellow and brown, particularly if the salts are impure. Solutions of radium salts have a blue luminescence, and the salts are all luminous in the dark. The spectrum of radium is characteristic, and it exhibits lines which belong to no other known element. Radium salts impart a crimson coloration to Bunsen's flame.

The chemical effects of the radiations from radium.—The Becquerel rays evolved from radium chloride closely resemble those from uranium and they produce similar effects, but over a million times more intense. The Becquerel rays from radium chloride or radium bromide incite phosphorescence in diamonds, rubies, fluorspar, calcium sulphide, zinc sulphide, barium platinocyanide, etc. If the eyes be closed, and a tube of radium bromide be held near the forehead, the retina of the eye becomes phosphorescent, and light will be seen though the eyes are closed. A tube containing a little radium bromide when held near the skin for a few hours produces painful sores. Caterpillars and other small animals are said to be killed if shut up in a box with a minute fragment of radium. The radiations coagulate proteid matter—*e.g.* globulin. It is also claimed that the exposure of malignant skin diseases, superficial cancer nodules, etc., has proved beneficial in many cases, although the testimony of medical experts is not unanimous. Becquerel rays cause chemical action—discolour paper and glass; turn oxygen into ozone; form hydrogen peroxide in acid, neutral, or alkaline solutions; decompose water; convert yellow phosphorus into the red variety; reduce mercuric to mercurous chloride, and ferric to ferrous sulphate; decompose iodoform, potassium bromide, hydrogen sulphide, carbon dioxide, etc. An aqueous solution of a radium salt continuously evolves hydrogen and oxygen gases, owing to the decomposition of the water. The radiations affect photographic paper, and discharge an electroscope as already indicated.

The action of a magnet on the radiations from radium.—A few sheets of paper or a couple of sheets of aluminium foil will cut off a large part of the radiations, and a sheet of lead, about half a centimetre thick, will cut off nearly all the radiations. A residuum still remains unsuppressed even after passing through 15 cm. of lead or through a far thicker block of iron. Hence, the radiations from radium are not homogeneous. Again, the radiations from radium are not affected in the same way by a magnet. Some of the rays are not influenced, for they do not bend when placed in a magnetic field; these are called the γ-rays. Others are bent *towards* the magnet, and are called the β-rays; while others are bent *away* from the magnet, and are called the α-rays. The three distinct types of rays in the radiations emitted from radium salts are as follows:

1. Alpha rays.—The α-rays are slightly bent by intense magnetic forces; they have a positive charge; and slight penetrative power, so that they are suppressed by a few layers of paper or a few cm. of air. The general properties of the α-rays correspond with those of the canal

rays in a vacuum tube The experimental evidence leads to the inference that the α rays are streams of positively charged electrons projected from radium with a velocity approaching 20,000 miles per second The emission of α particles from radium salts can be illustrated very neatly by W Crookes' spinthariscope A small fragment of a radium salt supported at the tip of a wire, *B* (Fig 318), in front of a screen, *A*, coated on the inside with zinc blende, is viewed in the dark through a magnifying eyepiece, *E*, which is focused on to the screen by sliding it up or down the tube Flashes of light are continually scintillating on the screen R K. Duncan likens the effect to the appearance of a swarm of fireflies on a dark night The scintillations are caused by the rain of α particles from the radium salt on to the screen Each impact is marked by a flash of light Each α-particle is supposed to produce one flash.

Fig 318 —Spintharoscope

2 Beta rays —The β rays are readily bent by comparatively weak magnetic forces in the opposite direction to the α-rays The β rays have a negative charge, and a stronger penetrative power than the α rays The general properties of the β-rays correspond with those of the cathode rays of the vacuum tube, for they appear to be negatively charged electrons or corpuscles projected from the radium salt with a velocity approaching 100,000 miles per second The corpuscles in Crookes' tube travel a little faster than the β rays from radium A difference in speed might be expected from their different modes of generation The following experiment—R J Strutt's radium clock—illustrates the character of the β rays A morsel of a radium salt is enclosed in a glass tube, *A*, Fig 319, coated with a conducting material and ending at the bottom with a brass cap from which hang a pair of gold leaves This system is fitted within a glass tube from which the air is exhausted The inside of the tube is coated with strips of tinfoil, *B*, connected with the earth by the wire, *C* The β rays from the radium pass through the glass and leave the central system with a positive charge This causes the gold leaves to gradually diverge until they touch the tinfoil, when they are discharged, and the leaves collapse The process begins anew This charge and discharge goes on continuously since the radium can emit these radiations an indefinitely long time This arrangement is perhaps the nearest approach yet made to perpetual motion The frequency of the cycle, of course, depends upon the amount of radium in the inner tube

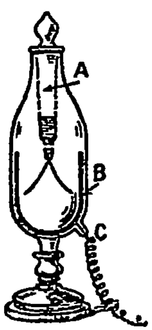


Fig 319 —Strutt's Radium Clock

3 Gamma rays —The γ rays are not affected by the most intense magnetic forces Their penetrative power is very intense, and they can manifest their presence after passing through several inches of metallic lead or several feet of metallic iron The relative penetrative powers of the three types of rays for aluminium are roughly as $\alpha : \beta : \gamma = 10 : 10^3 : 10^5$ The γ rays do not appear to be material particles at all, but the experimental evidence shows that the γ rays are similar to, if not identical with, Rontgen rays A diagrammatic illustration of the three types of radiation from radium can now be given, Fig 320 A piece of radium is

supposed to be placed in a lead vessel, A, sufficiently thick to prevent rays travelling through the walls Under the influence of an intense magnetic field, the rays no longer travel in straight lines, but they are deflected as shown diagrammatically in the figure

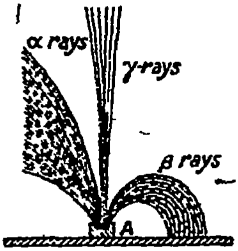


FIG 320 —Diagrammatic Analysis of the Radium Radiations by a Magnet

The spontaneous degradation of energy by radium —All three types of rays are continuously emitted by radium compounds in their normal condition The intense radioactivity of radium appears to be associated with the fact that the temperature of the salts is always a little—about 1 5°—above the temperature of their surroundings Normally, one gram of radium appears to evolve enough energy to raise a little more than its own weight of water from freezing to boiling point every hour, this amount of heat is equivalent to 118 cals per hour, or about 1000 cals per annum It has been estimated that a gram of radium will continue radioactive for about 2500 years, and it therefore follows that a gram of radium gives energy equivalent to that obtained by burning $\frac{8}{10}$ths of a ton of coal during the period of radioactive change Otherwise expressed, radium furnishes 250,000 times as much energy as is given by burning an equal weight of coal Obviously, too, a relatively large amount of energy is needed for the continuous decomposition of water by radium salts in aqueous solutions Hence radium is continually doing work at an undiminishing speed without any external supply of energy, otherwise expressed, the reaction is exothermal Whence comes this supply of energy ?

§ 7 The Degradation of Radium

All things have their emanations —EMPEDOCLES

Matter, formerly regarded as inert and only able to give back energy originally supplied to it, is, on the other hand, a colossal reservoir of energy—infra-atomic energy—which it can expend without borrowing anything from without —G LE BON (1908)

How does the continuous evolution of heat by radium agree with the dogma that heat cannot come from nothing, but must come from some other source ? The heat of a stove is derived from the oxidation of the fuel inside, with radium, it is assumed that the atoms (or molecules) are continually changing If radium be an element, and the radium atoms are changing into something not radium, it follows that there must be some flaw in the hitherto universally accepted definition of an element

According to P and S Curie

Any substance placed in the neighbourhood of radium acquires a radioactivity which persists for many hours and even days after the removal of the radium This induced radioactivity increases with the time during which it is exposed to the action of radium up to a certain limit After the radium is removed, it decreases rapidly and tends to disappear The kind of substance exposed to the radium is almost a matter of indifference, for all substances acquire a radioactivity of their own

This fact has been traced to the continuous evolution of a substance from radium which behaves as if it were a radioactive gas The emanation

emits only the α rays, that is, positive ions virtually as large as atoms themselves To avoid the hypothesis implied by calling the radioactive substance a "gas," E Rutherford, its discoverer, called it an *emanation*

The radium emanation is quite distinct from the three types of rays emitted by radium and its salts The amount is very small, but the supply is continuous If the temperature be raised the absorbed emanation is given off, for a short time, much more copiously than in the cold There is now little doubt that it is a gas, for it has a characteristic spectrum, somewhat resembling the spectrum of xenon, it can be condensed by liquid air to a minute drop of liquid (microscopic) of specific gravity 5 7, and at still lower temperatures, the liquid solidifies The solid melts at about $-71°$, and the liquid boils at about $-62°$ The radioactive gas is chemically inert, for it resists attack by every chemical reagent hitherto tried, it has a characteristic spectrum, and distinctive chemical and physical properties, and in consequence, the radium emanation has been placed with the argon helium group of the periodic table The atomic weight of the emanation, if it has an atomic weight, appears to be nearly 222 5 ($H_2=2$) This has been determined by the gas density, the diffusion, and the effusion methods It has been suggested that the gaseous radium emanation be called niton, Nt, from the Latin *nitens*, shining

The emanation, if kept by itself, slowly disappears After about four days, only about half the original quantity remains In fact, the radium emanation decomposes, continuously and spontaneously, into a radioactive solid and helium gas This latter observation is important Rutherford enclosed some radium emanation in a thin walled glass tube surrounded by a vacuum jacket, Fig 321 Each vessel was gastight, α rays from the radium emanation could penetrate the walls of the inner vessel, but not the walls of the outer tube By raising the left mercury reservoir, the gas in the annular space could be compressed in the spectrum tube, and there sparked, and examined spectroscopically In two to six days' time, a gas with the spectrum of helium accumulated in the annular space between the two tubes To show that the helium was not derived by diffusion from the inner tube, the emanation was removed and helium substituted No trace of helium could be detected in the outer vessel after standing several days This and other experiments have proved that the radium passes into helium viâ the emanation Otherwise expressed, helium is one decomposition product of radium Still further, the α-rays are streams of positively charged particles, each particle carries two unit positive charges, and each α-particle is an atom of helium carrying two unit positive charges

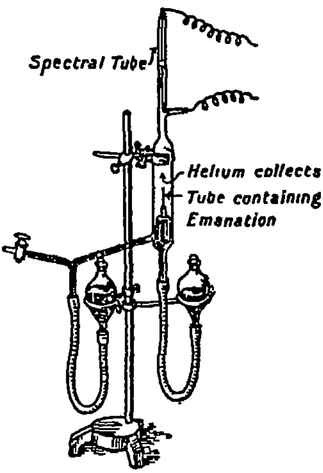


FIG 321 —Rutherford's Experiment showing the change of α particles into Helium

The action of the radiations on air —The movement of the swiftly speeding α particles is obstructed as they pass through a gas, and the

kinetic energy (p 111) is expended in doing work on the gas The gas into which the α-particles are discharged becomes a conductor of electricity, and it acquires a greater chemical activity The gas is said to be ionized The α-particles can travel but a few centimetres before their initial velocity is exhausted, and they pass into ordinary molecules of helium In air, for instance, the α particles from uranium are slowest—they can travel about 2 5 cm —whereas the α-particles from thorium C_2 travel fastest—about 8 6 cm

The career of the α-particles has been investigated at different stages of its flight At the beginning, when the speed and kinetic energy are greatest, the particle does *least* work in ionization It is supposed that just as a swiftly speeding bullet can cut a clean hole in a pane of glass, while a slowly moving bullet will shatter the glass, so when the speed of the α-particles is greatest, they can pass right through the molecules of a gas without producing any appreciable effect, but towards the end of their flight the ionizing power is greater because of the greater shattering power of the slowly moving molecules, and finally the particle ceases to ionize the gas and settles down to " ordinary life " as a helium molecule (or atom) The stopping power of a gaseous medium is determined, not by the physical or chemical properties of the gas, but solely by its molecular weight

The path of the ray through a moist gas has been made visible, owing to the condensation of water about the ions produced in the track of each α-particle C T R Wilson (1912) has photographed the fog so produced in the tracks of the α-particles, and the photographs make it very plain that the ionizing power of the particles rapidly reaches a maximum, and then rapidly sinks to zero as the molecules of helium Similar fogs produced by the β-rays have been photographed If a β-ray moves rapidly it produces a straight track, but the slower moving rays have more or less tortuous tracks, being deflected hither and thither by collision with the molecules of the gas The tracks produced by the Rontgen rays closely resemble those produced by the β-rays, and it is presumed that the Rontgen or γ-rays excite β rays in matter on which they fall, and that the effects produced by the γ-rays are directly due to the β-rays to which they give birth

Counting the α-particles emitted by radium.—E Rutherford and H Geiger (1908) devised an electrical method for counting the α-particles.

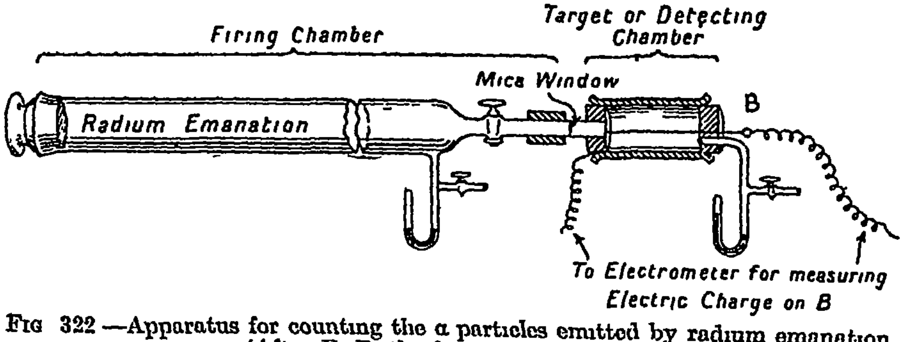


FIG 322 —Apparatus for counting the α particles emitted by radium emanation (After E Rutherford and H Geiger)

A small disc with a little emanation was fixed to a small iron cylinder and placed in a long glass cylinder—Fig 322 The position of the

radium disc could be adjusted by means of a magnet. This chamber—called the *firing chamber*—had a small mica window opening into a brass cylinder with ebonite ends and fitted with a central wire, *B*, connected with an electrometer. The brass cylinder was exhausted, and it then forms the target or *detecting chamber*. It was found possible to adjust the conditions so that two to five particles per minute passed through the mica window and upset the electrical equilibrium of the testing chamber. Each particle signalled its arrival by an unmistakable jump of the needle of the electrometer. The needle can be arranged so that its movements are recorded on a chart (Fig. 323). Each jump represents the arrival of one particle in the "detecting chamber." Some of the jumps show that two particles sometimes arrive simultaneously or almost simultaneously. Given the size of the window and the distance of the source of the projectiles, simple arithmetic furnishes the number shot per minute in all directions from the radium emanation. The results were consistent with those obtained by counting the number of scintillations produced per minute when a zinc sulphide screen was used as a target, and show that about 3.4×10^{10} of α particles are shot per second from a gram of radium. Each

FIG. 323.—Chart showing movements of the needle of the electrometer on the arrival of α particles.

α particle represents one atom of helium. Further experiments also showed that a gram of radium furnishes about 0.158 c.c. of helium per year, hence the weight of an atom of helium can be computed.

The restoration and decay of the radioactivity of radium.—The radium from which the emanation has been abstracted loses about 75 per cent. of its radioactivity and it then emits practically nothing but the α-rays; the β- and the γ-ray activities are almost completely lost. The normal radioactivity of radium gradually returns to its original value on standing. The rate at which the exhausted radium regains its activity is equal to the rate at which the emanation loses its radioactivity. Hence it is inferred that radium is constantly generating and storing the emanation, and that the emanation is constantly decaying. We have here the principle of opposing reactions, and the radioactivity of normal radium is an equilibrium value because the rates of production and disintegration of the emanation are evenly balanced. The processes of decay and restoration cannot be influenced by any known controllable physical or chemical force [1]; they are independent of the chemical form of radium—chloride, bromide, carbonate, sulphate, metal, etc.; all we can do is to study the mode and measure the rate of change. Hence, rightly or wrongly, it has been inferred that the process is a property of the radium *atom* alone; that the radium atoms break down into atoms of the emanation; and the atoms of the emanation break down into a radioactive solid

[1] This has, of course, no reference to the statement in the text to the effect that the emanation can be driven off from radium with a greater velocity at elevated temperatures because the emanation is already there. The rate at which the radium "manufactures" the emanation is not affected by temperature, etc.

and helium gas. This reminds us of the step by step decomposition of potassium hypochlorite into potassium chlorate, perchlorate, and chloride as well as oxygen. By analogy with the evolution of heat which attends certain exothermal chemical reactions—*e.g.* the decomposition of ozone $2O_3 \rightarrow 3O_2 + 68.2$ Cals.—it has been stated as an hypothesis that the origin of the energy of radioactive bodies is due to the decomposition of the atoms into electrons. In the one case, the atoms liberated during the reaction recombine to form new and more stable molecules; and in the other case, the liberated electrons unite to form new and more stable atoms. According to this hypothesis, a radioactive substance must have a more or less limited period of existence or life.

The products of the decay of radium.—The solid radioactive deposit has been studied, and it has been found to "decay" into a series of products some of which give α-, β-, or γ-rays, and the presence of the radioactive solid is therefore the source of the β- and the γ rays of radium. Hence, radium normally contains all three products—radium proper, the emanating gas, and the radioactive solid. It is estimated that 25 per cent of the radiations of normal radium belong to radium proper; 18 per cent more of the α rays belong to the emanating gas; and the remaining 57 per cent to the radioactive solid. The products of the decay of radium—radium-A, radium-B, etc.—so far as they have been at present made out, are as follows:

THE DESCENDENTS OF RADIUM

Radium	A →	B →	C_1 →	D_1 (1.4 min., β- and γ) / D_2	E_1 / E_2 →	F
Average life[1]	3 m	26.8 m.	19.5 m	15 y ?	4.8 d	140 d
Radiation	α-	β-	α-, β-, γ-	β-	β-, γ-	α rays
Estimated atomic weight	218	214	214	210	210	210

Helium is undoubtedly formed at each stage of the degradation. Radium-F appears to be the same as S. Curie's radioactive polonium which, in the absence of proof to the contrary, is thought, on further change, to pass into lead.

F. Soddy and H. Hyman (1914) tried if the atomic weight of lead extracted from the mineral thorite and ordinary lead showed any difference. They reported that the former gave the smaller result though no special precautions were taken to eliminate silver. M. Curie (1914) similarly found that lead derived from pitchblende had an atomic weight 206.5 when galenic lead had the value 207.01. Hence, it has been inferred that "there are several varieties of lead of different atomic weights determined by the initial metal from which they are derived." In general, lead derived from radioactive minerals has a lower atomic weight than ordinary galenic lead. T. W. Richards and R. P. Calvert (1914) add:

The inference seems to be that radioactive lead contains an admixture of some substance different from ordinary lead, and very difficult to separate from it by

[1] The term "average life" employed in the study of radioactivity corresponds with the following illustration: "If a church at a fixed time contains a number of people of different ages, then, given the number of years each person will live after leaving the church, the average life of the congregation is reckoned from the time fixed by that church attendance." This is not the average life taken from the time of birth used in computing insurance rates.—A. T. CAMERON (1910).

chemical means This substance cannot be identified in the ultra violet spectrum of the material, either because it has the same spectrum as lead, or because it has no spectrum in that part of the field, or because its spectrum is masked or absorbed by that of lead

With the elements copper, silver, iron, sodium, and chlorine from widely different sources no such difference in the atomic weight has been observed

THE DESCENDANTS OF THORIUM

	Thorium emanation →	A →	B →	C_1 →	D
Average life	54 sec	0 14 s	106 h	60 m	3 m
Radiation	α-	α	β-	α-	β γ-rays
Estimated atomic weight	220	216	212	212	208

With thorium, bismuth is said to be the hypothetical end product. The *onus probandi*, or burden of proof, of course rests with those who make the assertion Inability to prove a statement is false is rarely of much value as evidence that the statement is true

R W Gray (1913) reports that he found lead in some capillary tubes in which a minute quantity of radium emanation had been stored for four years There are three possible sources of the lead (*a*) The glass of the tubes contained 0 03 per cent of lead, (*b*) The mercury used to seal the tubes contained a trace of lead, (*c*) the disintegration of the emanation, *à la* the emanation hypothesis The glass of the tube was undoubtedly attacked by the emanation as shown by the discoloration, although no measurable amount of lead was obtained by digesting the powdered glass with water for some time

§ 8 The Degradation of Uranium

> The habit of suspending judgment until the conclusion has been fully tested by varying the circumstances of the experiment, and by repeated accurate measurement, is a valuable habit to acquire —G F FITZGERALD

Under ordinary conditions, uranium and its salts—presumably freed from radium—give both α- and β rays If crystals of uranium nitrate, $UO_2(NO_3)_2.6H_2O$, be shaken with aqueous ether, the lower aqueous layer contains uranium which gives the α- and the β rays, while the upper ethereal layer contains uranium which gives the α radiations only In order to distinguish these two varieties of uranium, the former is called uranium-X, and the latter simply "uranium" or "uranium proper" Uranium regenerates the normal quantity of uranium X in from six to twelve months Uranium X is responsible for the β rays of ordinary uranium, uranium proper gives only the α rays The extracted uranium-X loses its power of emitting the β rays at the same rate as uranium proper regains it A second quantity of uranium X can be extracted from restored uranium, and so also a third and fourth extraction can be made, and, so far as we can guess, the extraction, restoration, and re extraction can be repeated an indefinite number of times, that is, until all the uranium has been transformed into uranium X Hence, it seems impossible to avoid the inference that uranium is continuously and spontaneously decomposing into uranium X and helium In a similar manner it has been shown that uranium-X is itself breaking down into a radioactive solid which has been called ionium. Ionium bears some analogies with thorium.

Still further, it has also been proved that ionium is continuously and spontaneously passing into radium Consequently, starting from uranium,

	Uranium →	Uranium X →	Ionium →	Radium
Atomic weight	238 5	230 5	230 5	226 5
Average life	8,000,000,000 y	35 5 d	over 50,000 y	2500 y

There is some evidence that what is here called uranium is itself a mixture of what have been called uranium-I and uranium-II, but that these substances are so much alike that no method of separation has yet been successful There is some evidence that uranium-X furnishes two different products, uranium-X_1 and uranium-X_2. Without entering into further details, it can be said that there is a possibility that *uranium is a parent ancestor of radium, and radium is a parent ancestor of helium*, and, if inference be correct, that radium is the parent of lead Summarizing these changes on a kind of family tree showing the nature of the rays emitted, the atomic weights of the products, and the average life

GENEALOGICAL TREE OF THE URANIUM RADIUM FAMILY

Rays	Average life	Product
		Radium
↓ α rays	(5×10^9 years)	↓ Uranium (238 5)
↓	(10 6 years)	↓ Uranium$_2$ (234 5) → Ur_1 γ)
↓ α rays	(24 6 days)	↓ Uranium X (230 5)
↓ β- and γ rays	(2×10^5 years)	↓ Ionium (230 5)
↓ α and β rays	(2000 years)	↓ Radium (226 5)
↓ α rays	(3 85 days)	↓ Emanation (222)
↓ α, β, and γ rays		↓ Radium A to E
↓ α, β, γ rays		↓ Polonium
		↓ Lead (?)

GENEALOGICAL TREE OF THE THORIUM FAMILY

Rays	Average life	Product
α rays	(3×10^{10} years)	Thorium (232)
↓ rayless	(5 5 years)	↓ Meso thorium$_1$ (228)
↓ β γ rays	(6 2 hrs)	↓ Meso thorium$_2$ (228)
↓ α rays	(2 years)	↓ Radio thorium (228)
↓ α β rays	(3 7 days)	↓ Thorium X (224)
↓ α rays	(54 seconds)	↓ Emanation (220)
↓ α-, β, γ rays		↓ Thorium A to D
↓		↓ ?

Genealogical Tree of the Actinium Family

		Actinium
α, β rays	(19.5 days)	Radio-actinium
α rays	(10.5 days)	Actinium X
α rays	(3.9 seconds)	Emanation
β rays	(36.1 minutes)	Actinium A
α rays	(2.15 minutes)	Actinium B
β, γ rays	(5.1 minutes)	Actinium C
		?

Curiously, also, potassium and rubidium are slightly radioactive, for they emit β rays, while the radioactivity of sodium has not been detected. Therefore, between 30 and 40 radioactive bodies are assumed to exist; not half a dozen of these bodies have been isolated. The properties of those radioactive elements which have not been isolated have been deduced from their behaviour when mixed with large proportions of other known elements.

We have seen that the atomic weight of radium is 226.5 and of the emanation 222.5. It therefore follows that one atom of radium furnishes one atom of the emanation and an α particle which, in turn, furnishes an atom of helium with an atomic weight 4. No other material product of the change is known, and the reaction is accordingly symbolized

$$\text{Radium} \longrightarrow \text{Emanation (i.e. Niton)} + \text{Helium}$$

Similar assumptions have been employed in estimating the atomic weights of the other radioactive substances. The emission of β rays (*i.e.* electrons) is supposed to produce no measurable change in the atomic weights, while the emission of α rays (charged helium atoms) at each stage of the disintegration is supposed to reduce the atomic weight by 4.

At the beginning of 1913, several investigators stated that the expulsion of an α-particle by a radioactive element causes the residual product to shift its position two "places" in the periodic table in the direction of diminishing mass, so that the residual product is not in the next family, but in the next but one. Similarly, when an element gives off a β particle, the product shifts its position in the opposite direction one "place" in a direction opposite to that for an α ray change. Hence two changes attended by the emission of β particles, and one by an α particle would bring the product back to its original position in Mendeléeff's table. Further, when any number of radioactive elements occupy one place in the periodic table, these elements cannot be separated from one another by any known chemical process. Thus, when mesothorium-I gives off two β particles and one α particle to form thorium-X, it is claimed that the two substances cannot be separated from one another in spite of the difference in their atomic weights; and they are probably spectroscopically

indistinguishable F Soddy (1913) calls these non-separable elements isotopic elements, or isotopes, *e g* ionium, thorium, and radio-thorium are isotopes, and meso-thorium is isotopic with radium The different forms of lead discovered by Soddy connected with radioactivity (1914) are also said to be isotopic, for they have the same atomic volumes and the same chemical properties, but F A Lindemann (1915) has shown that two elements of different atomic weight must differ either in their chemical or physical properties The argument is based on the laws of thermodynamics, and he argues that the lead from thorite will probably have a melting point 1 54° higher than ordinary lead

To summarize, the more salient *facts* are

(1) Radioactive substances are decomposing spontaneously

(2) The reaction is exothermal, but the speed of the decomposition is not affected by any known external condition, the thermal value of the reaction, too, is more than a million times greater than that of any known chemical reaction

(3) The decomposition proceeds in a series of stages—consecutive reactions

(4) Helium is one ultimate product of the decomposition

(5) Three types of "radiant rays" are emitted at different stages of the decomposition

The occurrence of radioactive substances —Radioactive substances—chiefly thorium and radium—occur in many minerals in comparatively large amounts In the uranium minerals, for example, the ratio Ra U averages nearly 3 5$\times 10^{-7}$ by weight Radioactive substances are everywhere present in the atmosphere It is estimated that a million parts of atmospheric air contain 0 06$\times 10^{-12}$ parts of radium emanation, and 2$\times 10^{-18}$ of thorium emanation Hence, a charged electroscope in an exhausted glass vessel may retain its charge for months, but if air be admitted, the instrument will be discharged in a relatively short time—say, 24 or 36 hours The emanations are found more particularly in the atmosphere over land than over the sea Hence, it is inferred that the radioactivity of the atmosphere is derived from emanations from the land, and this is in agreement with the fact that the radioactivity of deep-sea water is greater near the bottom than near the surface So far as observations have been made, every cubic centimetre of sea water averages about 0·017$\times 10^{-12}$ grm of radium This means that not less than the equivalent of 20,000 tons of radium occurs in the oceans of the earth Radioactive substances are widely distributed in the solid crust of the earth, they are found in all kinds of rocks, clays, soils, etc One estimate indicates that an average of 1 4$\times 10^{-12}$ grm of radium is present per gram of rock The water from deep seated springs and wells has usually a marked radioactivity, and it has been stated that the curative properties of certain mineral waters—*e g* those of Buxton, Bath, Wiesbaden, Bohemia, etc —are due to their radioactivity This statement is mere guessing, because so little is known about the physiological action of the radiations from radioactive materials The fact that radioactive substances constantly emit heat, and since the emanations are ubiquitous in the earth's crust, it follows that the heating effects of these substances must play an important part in maintaining the heat of the earth, and must have profoundly modified the rate of cooling of the earth in past ages

The Mutability of the Elements, and the Disintegration of Atoms

> To inquire whether the metals be capable of being decomposed and composed is a grand object of true philosophy —H DAVY (1811)
>
> Radioactivity is the least manageable of natural processes It will not be hurried or controlled Nature keeps the management of this particular department in her own hands Man views the phenomenon with hungry eyes, but his interference is barred out He can only look on in wonder while it deploys its irresistible unknown forces —ANON (1907)

About 1902, many hypotheses were suggested to explain the phenomena associated with radioactivity, R Meldola, for example, suggested the helide **hypothesis of radioactivity** In this, the radioactive elements are supposed to be compounds of helium with other elements—helides—and these compounds are further supposed to be undergoing a gradual spontaneous decomposition into simpler substances This hypothesis has been abandoned by R Meldola, it has received very little consideration, because attention has been mainly focused upon a second hypothesis, which runs somewhat as follows Ordinary atoms are supposed to be small intricate systems of electrons, linked together by forces of tremendous power The properties of the different elementary atoms are determined by the number and configuration of the intra atomic electrons Radioactivity is an atomic property, and it is an effect of the instability of certain atomic systems The disintegration of the unstable atoms is marked by the emission of rays The radioactive elements are therefore unstable, and are continually and spontaneously changing by numerous intermediate stages into more stable elements This hypothesis is called **Rutherford and Soddy's theory of the disintegration of the atoms**, because they established its claim to serious consideration, and have done valuable work with its aid Their hypothesis is orthodox and fashionable If this hypothesis should survive that struggle for existence which all neoteric hypotheses must undergo, then radioactivity will be cited as proof of the **devolution of the elements** Astro spectral observations, p 822, leave little room for doubt that in the "cooling stars" a process of **evolution of the elements** is in progress

It is further assumed that the radioactive elements are not unique among the elements in containing abnormal stores of internal energy, but —excluding potassium and possibly rubidium—the other elements are either immutable or else they are changing so slowly that no signs of mutation have yet been detected According to the atom disintegration hypothesis of radioactivity Nature is continually changing the elements with the largest atomic weights such as uranium (238 5) and thorium (232 4) into simpler elements The latter, in turn, are said to be stable simply because no signs of radioactivity have yet been detected. It is possible that if ever elements existed on earth with larger atomic weights, and by inference, with more complex atoms, they have all degraded into simpler forms, and are now probably extinct elements, hence, also, it might be inferred that *the most widely diffused elements have small atomic weights* The gaps which appear in Mendeleeff's table (p 808) also appear significant The elements with the smallest atomic weights, and those which are found in greatest abundance on the earth—hydrogen, helium, calcium, oxygen, sodium, silicon, etc —are usually considered to be the most stable, and to

contain least infra atomic energy Hydrogen and helium, occurring in the hottest stars, are supposed to have a tendency to form aggregates, and pass into common terrestrial elements during the cooling of the hot stars. It seems as if uranium and thorium must have been exposed to peculiar conditions—possibly of pressure and temperature—whereby they were elaborated beyond the limits of stability, and absorbed stores of energy which are now being slowly released because the conditions necessary for their stability no longer obtain

It might be asked why the comparatively conspicuous self-destructive activities of radium have not led to its extinction long ago? Rutherford estimates that the radium now on earth will be disintegrated and the whole virtually extinct in about 25,000 years There can thus be little doubt that if there had not been a continuous source of supply, radium would have been an extinct element long ago The decay of the heaviest known element uranium is so extraordinarily slow that it can just be detected, and a rough estimate made of its life—8,000,000,000 years—as indicated above.

The mode of evolution of the elements hypothecated in the attempt to co-ordinate the results of the spectroscopic study of stars and nebulæ, seems to be supported by a mass of cumulative evidence (p 817), and to be inherently probable It remains to find an adequate explanation to account for the vast stores of energy available in the hotter stars Here again we are confronted with mystery profound (p 123)

The distribution of the elements —The reasons for thinking that the supplies of radium are continually renewed turn on the facts

1 Radium and uranium always occur together, and the two elements are not sufficiently common for this to be due to mere chance, and

2 The proportion of radium to uranium in the uraniferous minerals is almost invariable—1 35,000,000 This approximate constancy is clearly the result of an equilibrium between production and decay The supply of radium is regulated by its relative rates of formation and degradation, and when the speeds of the opposing reactions are balanced, the ratio radium uranium must be constant It is interesting to observe in this connection that a very small amount of helium is always found occluded in uraniferous minerals Assuming that no helium escapes, the small amount found in a given rock will be a measure of the time which has elapsed since the birth of that particular sample, but this gas must be constantly leaking into the atmosphere, and, consequently, the "age" so computed will be a minimum age of the mineral for the mineral may be older, but not younger than the age so computed Hence, by determining the relative amounts of uranium and helium in a mineral, its minimum age can be estimated In this way, Strutt estimated that it requires eleven million years to produce one c c of helium per gram of uranium Lead also has been detected in over forty uraniferous minerals, and in many of these cases lead does not occur near the uranium deposit Hence it is considered unlikely that the lead has been deposited about the uranium by subterranean streams The general notion is that lead is the "final" product of the degradation of uranium (p 845), in spite of the fact that the change is too slow to be observed directly, and the evidence very flimsy

We can now see a possible explanation for the "inseparable companionship" of many elements emphasized on p 818 The "occurrence" or "distribution" of the elements over the earth appears to be an effect or

an important genetic law The approximate uniform quantities of many of the rarer metals in different parts of the earth indicate that these elements are degradation products of more complex elements, and that they, in turn, will probably be degraded into simpler products The relative speeds of these slow changes determine the amount of each element which can be present on the earth at any given time

The student may very properly think that *a modicum of fact is here entangled with an abnormal amount of speculation*, especially when it is remembered that the experiments have been made upon very minute quantities of material. At first sight, it does appear as if we have developed what A Smithells humorously called "a chemistry of phantoms" Thanks, however, to the extraordinary delicacy of the electrometer and of the spectroscope, there is no doubt about the facts, even though but extremely minute quantities of radium are available for experiments The argument converges on the assumption that radioactivity is an atomic property, this hypothesis, in turn, is mainly based on the indifference of the speed of radioactive changes to external conditions of temperature, pressure, etc It is therefore pertinent to inquire into the validity of the alternative hypothesis, and ask

Are the "radioactive elements" really elements, or are they compounds containing helium? As already hinted, the dogma that radium is an element is not so firmly established that there are no reasonable grounds for the exercise of some Cartesian doubt (p 735), for, said E W Morley (1909), he is wise whose assertions regard the possibility of finding at some time evidence to the contrary E Rutherford (1909) has said that "since in a large number of cases the transformation of the atoms is accompanied by one or more charged atoms of helium, it is difficult to avoid the conclusion that the atoms of the radioactive elements are built up, in part at least, of helium atoms" As an alternative to Rutherford's atom disintegration hypothesis, and as a corollary to the inference that the molecules of the argon helium family are really polyatomic (pp 564, 659), R Meldola (1903) suggested that the radioactive elements are really compounds of an active form of helium in the same sense that nitrogen chloride may be said to contain the atomic or active form of nitrogen Ordinary helium, like ordinary nitrogen, is characterized by great chemical inactivity If this hypothesis be valid, it must be supported by a formidable list of unique hypotheses, for it must be assumed further that (1) the alleged compound—helide—is spontaneously decomposing, (2) abnormally large amounts of energy are set free during the decomposition, (3) the emission of radiations accompanies the change, (4) the speed of the decomposition is not affected by any known external conditions, and (5) in opposition to a little circumstantial evidence, that the helium molecule is a complex of atoms, and not monatomic *Otherwise*, adds H E Armstrong (1913) the decomposition of radium regarded as a compound of atomic helium is no more remarkable than that of liquid ozone, or of nitrogen chloride! Armstrong continues

The atoms of helium and of the allied inert gases are gifted with intense activity far beyond anything we know of, it may well be that when such atoms enter into combination, either with one another or with other elements, the amount of energy set free is very great and that when they combine with other materials, they may produce changes in properties very different from and far more profound than those we know of at present

The plausibility of the helide argument turns on this The greater the amount of hypothetical energy assumed to be required to break down the hypothetical helide molecule into its supposed atoms, the greater the appearance of probability of the argument that radioactive phenomena are chemical in kind Questions like these have to be treated more by instinct (or prejudice) than by logic, and those who do the work must use what hypotheses they find most fruitful.

H. S. Sheldon (1913) has emphasized the fact that the indifference of radioactive changes to temperature and other physical conditions must be a relative phenomenon, and a consequence of the limited range of our resources The highest temperatures of our laboratories—3000°—are feeble when contrasted with those ten times hotter, which prevail in the colossal furnaces revealed by stellar spectra of the hotter stars Consequently, the indifference of radioactive changes to external conditions cannot be accepted as absolute Suppose, he adds, that electricity were unknown and it was only possible to attain variations of temperatures of a few degrees in our laboratories, then a large number of so-called compounds would be classed as elements, and the slow decomposition of many substances with the evolution of heat would appear as marvellous sources of energy, as unaccountable as radioactive changes are to day

§ 10 The Effect of the Discovery of Radioactivity on the Definitions of Element and Atom.

> We must fight against the soporific influence of sham definitions Especially must we guard against ever allowing them to stand in the way of an inquiry into facts —A. SIDGWICK.

Naturally, the student of chemistry may be somewhat disconcerted with this apparent attack on what appear to be the essential principles of chemistry outlined in the earlier part of this text-book. At first sight, it seems as if we must say "good-bye to the equations of chemistry," because, if the truth about the suspected disruption of atoms be ever vindicated, it appears that the fundamental concepts—atom, element, persistence of weight, etc —must be revised in order to make them describe the facts

The elements —The conception of an element, given on p 12, has long held an honoured place in chemical text-books, and, with this before us, it certainly appears illogical to apply the term to a substance which can be resolved into two or more simpler forms of matter Any substance which can furnish two or more different elements has certainly forfeited its place in the list of elements Some try to evade the difficulty by assuming that there is an agreement among chemists to recognize a substance as an element which, under proper conditions, exhibits a spectrum showing characteristic lines possessed by no other element, and possesses a definite combining weight Of course, we are at liberty to change our definitions, but, as W Bancroft (1912) has said, the only advantage of the new definition is that it enables chemists to say that they have decomposed an element S Curie (1911) stated definitely that radium is not a compound of helium, but the only way she can make radium an element is by changing the old definition so that it shall not include radium The definition on p 12, however, is elastic enough to cover cases of transmutation, for, if an element containing but *one kind of matter* suffered an

atomic cataclysm, it might furnish two or more different kinds of matter each of which is an element because it contains but one kind of matter It would probably lead to clearer thinking if a special term were invented For example, some one has suggested that the elements be called *chemical primaries* We are always loath to multiply definitions, and would much rather condense a number of definitions into one, here, however, there seems a special need for distinguishing terms As already emphasized, the definition must not be taken to imply that the elements are absolutely immutable, although, so far as our present knowledge goes, they are both immutable and primitive

The atoms—Paradoxical as it may seem, the hypothesis that the atom of an element is a most intricate bit of mechanism, a complex aggregate of parts liable to disruption, is now generally accepted This, however, does not affect the time honoured definition of an atom indicated on p 36 The atom still remains a veritable unit indivisible in chemical reactions Had the facts, speculations, and theories discussed in these concluding chapters been treated at the beginning of our study, that would not have altered our mode of presenting the facts of material chemistry

The law of persistence of weight—Suppose an atomic convulsion or cataclysm were to occur so that the complex system of electrons which is supposed to form an atom were to break up into simpler parts, suppose further some of the electrons grouped themselves into helium, and the others into some other substance, and let us also assume, for the moment, that some electrons simultaneously escape and are merged into the æther of space, it is then conceivable that there will be an apparent loss of weight Consequently, while *the law of persistence of weight holds good with chemical reactions in which the atoms remain intact*, it is quite conceivable that an apparent loss in weight *might* occur during a radioactive change (p 7) If the products of the disintegration of the atom have mass, it might be inferred that the absolute mass still remains constant, although, if radium be an element, the invariability of mass or weight can no longer be referred back to the constancy of the atom This visionary phenomenon has been described in order to emphasize the need for care in building rigid, non-plastic concepts and definitions from negative results based on the uncontradicted experience of mankind, p 110

§ 11 The Transmutation of the Metals—Alchemy

Would to God all men might become adepts in our art for then gold, the great idol of mankind would lose its value and we should prize it only for its scientific teaching —E PHILALETHES (c 1623)

Alchemy appears to have been a medieval system of philosophy, and it sought to demonstrate the validity of its doctrines concerning the cosmos by transmuting the baser metals into gold The following excerpts from alchemical writings will perhaps make clear their ideas on this subject

Gold is the most perfect of metals because in it Nature has finished her work —ROGER BACON (1214–1294)

The metals are all essentially identical, they differ only in form Form brings out the accidental causes which the experimenter must try to discover and remove —ALBERTUS MAGNUS (1193–1284)

If by any reason the superfluous matter could be organically removed from the baser metals, they would become gold and silver Our art only arrogates to

itself the power of developing, through the removal of all defects and superfluities the golden nature which the baser metals possess —E PHILALETHES (c. 1623)

The mystic gnome who laboured in order to quicken the growth of the metals in mines was a creature of the superstition of the childhood of man. The, perhaps, more philosophical alchemists believed that the perfecting of the metals occurred spontaneously in the "bowels of the earth," and Pliny tells us that exhausted mines have been closed down to enable the metals to fructify, and so be again profitably worked in a few years' time They also believed that Nature aimed at the production of gold in mines, and that when she is hindered in her design, the so called imperfect metals appeared The baser metals were hence called "diseased gold", mercury was "ailing silver", copper, iron, lead, and tin were "lepers" which, when cured of their leprosy, would become gold The alchemists sought to find some means which would hasten the slow natural change so that the transmutation could be conducted in a much shorter time "It is this means," said Roger Bacon, "which the alchemists indifferently called the elixir, the philosopher's stone," etc

The alchemists wrote in a language we do not now understand They seem to have associated mystic extravagances with their operations, and to have described their processes in obscure ambiguous jargon, with the result that their readers were "stunned," as Boyle expressed it, "with dark and empty words" No wonder that J Potanus (1520) complained that after travelling through many countries to examine the claims of the adepts, he found "many deceivers, but no true philosophers", and N Lemery (1675) that "they professed an art the beginning of which was deceit, the progress of which was falsehood, and the end beggary" Alchemy thus fell into disrepute, for it seemed as if its claims could be established only by chicanery and fraud Some of the more honest believers explained their failure by asserting that "the art of making gold is beyond the reach of human capacity, and it is made known by God to those alone whom He favours, and who are called adepts" The majority of alchemists, however, did seek to make gold cheaply with the sole object of gaining "untold wealth" Failure or delusion was inevitable Accordingly, the alchemist often misrepresented the truth and degenerated into a charlatan and impostor, pretending with vulgar frauds, that he had succeeded "in order," says M M P Muir, "that he might really make gold by cheating other people," or else gain notoriety

The idea of transmutation appears to have come from the Egyptians and Chaldeans, but its real origin is lost in remote antiquity M Berthelot (1885) considers that the idea did not originate from the philosophical views of the ancients on the unity of matter as is stated above, but rather from the attempts of the goldsmiths to make fraudulent substitutes for the precious metals

It is easy to understand how the belief that the base metals could be converted into gold dominated ancient and medieval chemistry Facts were cited in its favour The production of beads of silver and gold by the cupellation of metallic lead, and the reduction of metallic ores furnished direct evidence of the metamorphosis of the metals Again, iron utensils in copper mines became coated with red copper when left in contact with the "mine water," so that the iron was seemingly transmuted into copper,

similarly, the formation of white and yellow alloys by mixing copper and certain earths, seemed with the then imperfect knowledge, ample proof of transmutation. The dogma of transmutation thus appeared eminently plausible; it ran counter to no known laws of nature; it rested upon no extravagant assumptions; and it was sanctioned by the highest authorities. The immense labour which must have been expended in the fruitless pursuit of this chemical chimera by the alchemists is appalling. The quest was virtually abandoned with the advent of Lavoisier's balance.

I. Remsen (1903) has emphasized the fact that the alchemists were the working chemists of their day, and that they laid the foundations of experimental science. He further develops the idea that there is a life after the death of a good doctrine. The phlogiston theory lived in the form of the modern doctrine of free energy, and the idea that there is a relationship between the elements is what Remsen calls the spiritual part of alchemy which lives though alchemy is dead.

The alchemist's dream of transmutation is little if any nearer realization to-day than it was a thousand years ago, for no one has yet really succeeded in transmuting one chemical element into another other than by speculative argument. There is no unimpeachable evidence of a single transmutation of one element into another pre-determined by man. In the words of S. Curie (1912): "on ne peut considérer qu'il y a pas encore actuellement de raisons suffisantes pour admettre que la formation de certains éléments puisse être provoquée à volonté en présence de corps radioactifs." True enough, a few radioactive elements—radium, actinium, polonium, uranium, and thorium—seem to have been discovered in nature, and they are usually stated to be changing spontaneously from one elemental form to another; but no process known to man is able to accelerate or retard, stop or start the metamorphosis. No element has yet been broken down into a simpler substance by a process controllable by man. "Nature to be conquered must be obeyed" (Francis Bacon).

The alleged transmutation of copper into lithium and sodium by A. T. Cameron and W. Ramsay (1908) has been denied by S. Curie and Gleditsch (1908) and by E. P. Perman (1908)—the lithium and sodium were derived from the vessels used in the work; the production of neon from radium emanation by W. Ramsay (1907) and W. Ramsay and A. T. Cameron (1908) has been denied by E. Rutherford and T. Royds (1908)—the neon was derived from the air which had not been excluded from the apparatus; and the formation of carbon dioxide by the action of radium emanations on solutions of thorium and zirconium by W. Ramsay and F. L. Usher (1909) has been called in question by E. Rutherford (1913)—the carbon appears to have been derived from the grease used in lubricating the stopcocks. The alleged transmutation of hydrogen into neon, by W. Ramsay (1913) and J. N. Collie and H. Patterson (1913) by the action of a stream of cathode rays on hydrogen is considered by J. J. Thomson (1913) to be a mal-inference, since the neon is thought to be derived from that originally occluded by the electrodes, or glass vessel, and which is expelled by the bombardment of the cathode rays, but which cannot be removed by the mere application of heat. R. J. Strutt (1914) and T. R. Merton (1914) could not verify the alleged conversion of hydrogen into neon.

Intra-atomic energy.—The facts previously indicated show that not far from 2,000,000,000 cals. of heat are evolved during the degradation of one gram of radium. This is a quarter of a million times greater than is evolved by the combustion of a similar weight of coal. Hence it is inferred, *from the atomic disintegration hypothesis of radioactivity*, that the atoms of the radio-active elements, and probably also of other

elements, have tremendous stores of potential energy, far greater than is developed during ordinary chemical reactions. The rate of degradation of the energy of the radioactive elements is comparatively slow, and is not available for doing useful work. The rate of evolution cannot be influenced by any known conditions and consequently the transmutation of the elements involves the discovery of methods of controlling these tremendous supplies of energy Just as the application of a large quantity of electrical energy concentrated at the ends of a pair of platinum wires enabled H. Davy (1808) to decompose the alkalis, so W Ostwald, W Ramsay, and others infer *if ever one stable element is transmuted into another element, a large quantity of energy in a highly concentrated condition will be required* This is quite in harmony with the alleged dissociation of the elements in the hotter stars (*q v*) where but a few elements are present, and where the temperature has been estimated at 25,000° The 3000°–4000° obtained in some electrical furnaces appear but puny in comparison with the tremendous natural powers present in the hotter stars—p 376

It has been pointed out that the formation of, say, gold from a metal atomically lighter, say tin, would require the expenditure of so much energy that even if the transformation were accomplished, it could not be a successful commercial process for the production of gold On the other hand, the formation of gold from an atomically heavier metal, say lead, would liberate such an enormous amount of energy that the gold would be but an insignificant by-product, for the energy liberated during the process would have an enormously greater value than the metal.

§ 12 The Creation and Annihilation of Matter

Even if we resolve all matter into one kind, that kind will need explaining And so on for ever and ever deeper and deeper into the pit at whose bottom truth lies, without ever reaching it. For the pit is bottomless —O Heaviside

Things which are seen were not made of things which do appear —St Paul.

Æther is the parent of all things —Lucretius (*c* 60 B C)

In mechanics, the definition of matter is based upon Newton's first law of motion—the law of inertia—where matter is defined as that which requires the expenditure of an external force to change its state of motion Otherwise expressed, inertia, or helplessness, is a characteristic of every form of matter No material thing can of itself change its own state of motion, for an external influence is required before such a change can take place If it be admitted that any entity which requires the application of a force before it can change its state of motion is said to be a form of matter, an electron in motion must be a form of matter, because it requires the application of a force to change its state of motion

The inertia of matter —This definition is also reversed, and force is defined to be that influence which is required to change the velocity of any material body, and it is measured in terms of the dyne as unit A dyne is that force which applied to a mass of one gram during one second imparts to it a velocity of one centimetre per second, or which changes the velocity of the body one centimetre per second when acting for one second These ideas can be expressed in another form The inertia of a body is that property of matter which resists change of motion, and it is measured in terms of the force required to produce a change of one centimetre per second in the

velocity of the body. Accordingly, *when the action of a force on two bodies produces the same change of velocity per second, their inertiæ are said to be equal.*

The mass of matter.—A body falling from a height down to the earth's surface—*in vacuo* so as not to be influenced by the resistance of the air—gains in velocity, say, g cm. per second. If the mass of the body be m, then the force pulling that body down will be measured by the product mg. This is the weight of a body; hence the weight of a body is g times its mass. The weight w of a body measures the force by which it is attracted to the earth's surface, whereas mass refers to the quantity of matter m in a body, and is independent of gravitation or weight. Experiments have shown that all material bodies have the same numerical value for g, namely, 981 cm. per second when acting for one second (latitude 45°, and at sea level). Accordingly, $w = 981m$, or the weight of one gram of matter is 981 dynes; or the weight of a body is 981 times its mass; or the mass of a body is $\frac{1}{981}$ of its weight—under standard conditions. The masses of two bodies in the same place must therefore be proportional to their weights. *If in the same locality the action of gravity on two bodies produces the same change of velocity per second, their masses are said to be equal.* This conclusion is in harmony with that deduced in the preceding paragraph, and, accordingly, it has been inferred that **mass and inertia are identical**; meaning that the definitions of inertia and of mass, in the nomenclature of mechanics, are not mutually exclusive.

Electromagnetic mass.—When charges of electricity are set in motion, they act like electric currents, and set up magnetic fields which oppose the motion—Lenz's law. Motion against the induction effects requires an expenditure of energy, and therefore a moving charged particle will appear to have an added electromagnetic inertia in virtue of its constituent charges. This added inertia will be proportional to the total electrical energy of the charges. H. Kaufmann (1906) measured the value of the numerical ratio e/m, where e represents the electric charge, and m the inertia or the mass, for electrons travelling at different speeds, and found—

Velocity $\times 10^{-10}$	2.83	2.72	2.59	2.48	2.36 units
$e/m \times 10^{-10}$	0.63	0.77,	0.97,	1.17	1.31 units

Hence, either the value of m *increases* or the charge e *decreases* with increasing velocity; for the greater the velocity the smaller the numerical value of the ratio of the electric charge to the mass. Rightly or wrongly, it is assumed that the charge on the particles remains constant and invariable, and accordingly, it follows that the (electromagnetic) mass of the electrons is not constant, but increases rapidly as the velocity is augmented. Further, if any part of the mass of an electron is ordinary mechanical mass, it must be very small in comparison with that which is of electrical origin, since the electrical inertia of a body depends upon its velocity and approaches infinity when the velocity of the body approaches that of light. This variation in the apparent inertia or mass of a body is the same as if the electrical mass existed alone, and the material mass were virtually zero. Consequently it has been inferred that (1) the electrons do not possess a material mass in the ordinary sense of the word; and (2) the electrons have no mass other than that which is derived from their motion and electrical charge. If the real mass of an atom is the sum of the positive and negative electrons, and the latter have no material mass, it might be inferred that

the positive electrons or the mass of an atom would still remain a constant, H A Lorentz, however, has shown that in all probability the masses of all particles will be affected by their translational velocity to the same degree as the electromagnetic mass of the electrons

Again, it is assumed that electricity is a phenomenon of the æther, and that the atom is built entirely of electrons , consequently, as J Larmor (1900) expressed it atoms are forms of æthereal strain, or the material atom is formed entirely of æther, and has no material substratum Further, the electrons are supposed to be minute electrified strains, squirts, vortices, swirls, eddies, or whirlpools in the æther The intangible, imponderable, all-pervading æther is supposed to be susceptible to the solicitations of gravity, as matter, only when it is stirred into innumerable swirls, which are held together by powerful cohesive forces Hence, it is said *æther is the mother of matter* , for in the æther—

> Wrapt in mystic silences and glooms,
> The slumb'ring secrets of creation lie

Some even claim to have created material atoms from immaterial æther, but the claims are somewhat questionable The stages in the alleged genesis and destruction of matter can thus be symbolized

$$\overbrace{\text{Matter } \textit{en masse} \rightleftharpoons \text{Molecules} \rightleftharpoons \text{Atoms}}^{\text{Material}} \rightleftharpoons \overbrace{\text{Electrons} \rightleftharpoons \text{Æther}}^{\text{Immaterial}}$$

$$\text{Dematerialization of matter} \rightleftharpoons \text{Materialization of æther.}$$

When, therefore, it is assumed that material electrons have been resolved into primitive æther by relieving the strains, or stilling the swirls, it is at the same time assumed that matter can be deprived of cosmical existence, and transmogrified into Nirvanian nothingness With the annihilation of ponderable matter, the law of the conservation of matter disappears, and apparently the only constant in the universe is nothingness !

The argument turns on the nature of the electrons and of the æther The æther is assumed to be immaterial, or, as Pythagoras (c. 500 B.C) expressed it, "a celestial substance free from all perceptible matter" As a matter of fact, the ætherial plenum cannot be compared with any known thing It is utterly beyond the range of our sense perceptions, and as G le Bon (1907) has said, we are related to the æther much as a man born deaf is related to music, or a man born blind is related to colour , accordingly, no analogy can make such men understand what is a sound or a colour In the words of T A Edison (1893) "As for the æther which speculative science supposes to exist, I know nothing about it."

§ 13 Thomson's Corpuscular or Electronic Hypothesis of Matter

> If we be curious to know what matter is, we plunge at once into that deep which surrounds us on every side, and which never yet was fathomed by human intellect —J F DANIELL.
>
> Liability to error is the price we have to pay for forward movement —A. SIDGWICK

No difference other than velocity of translatory motion has been detected in the properties of negative electrons when produced in many

TABLE LXIII

Total number of electrons	Number of electrons in successive rings (numbered onwards)				
	1	2	3	4	5
4	4				
5	5				
6	5	1			
7	6	1			
8	7	1			
9	8	1			
10	8	2			
11	8	3			
12	9	3			
13	10	3			
14	10	4			
15	10	5			
16	11	5			
17	11	5	1		
18	11	6	1		
19	11	7	1		
20	12	7	1		
21	12	8	1		
22	12	8	2		
23	13	8	2		
24	13	8	3		
25	13	9	3		
26	13	10	3		
27	13	10	4		
28	14	10	4		
29	14	10	5		
30	15	10	5		
31	15	11	5		
32	15	11	5	1	
33	15	11	6	1	
34	15	11	7	1	
35	16	11	7	1	
36	16	12	7	1	
37	16	12	8	1	
38	16	12	8	2	
39	16	13	8	2	
40	16	13	8	3	
41	16	13	9	3	
42	17	13	9	3	
43	17	13	10	3	
44	17	13	10	4	
45	17	14	10	4	
46	17	14	10	5	
47	17	15	10	5	
48	17	15	11	5	
49	17	15	11	5	1
50	18	15	11	5	1
51	18	15	11	6	1
52	18	15	11	7	1
53	18	16	11	7	1
54	18	16	12	7	1
55	19	16	12	7	1
56	19	16	12	8	1
57	19	16	12	8	2
58	19	16	13	8	2

different ways, and from many different gases, and since the mass of a negative electron (corpuscle) is less than that of any known atom, the corpuscle must be a constituent of many different substances, and the atoms of these substances consequently must have something in common This suggests the idea that the atoms of the chemical elements are built of simpler components the electrons have thus been regarded as the ultimate sub atoms or the *Uratomen* of which matter is essentially composed Since the electron is a constituent of atoms J J Thomson considers that "it is natural to regard the electron as a constituent of the primordial system" J J Thomson's electronic theory of matter is one of the unitary theories of matter It assumes that each atom of any element consists of a large number of electrons, all electrified negatively, and held together by positive electricity equivalent in amount to the sum of the negative charges of all the electrons so as to produce an electrically neutral atom Thomson also accepts the atom disintegration hypothesis of radioactivity

The distribution of a number of negatively charged particles in a sphere of uniform density has been investigated mathematically by J J Thomson (1904) Five is the greatest number of electrons which can be in equilibrium in a single ring But if other electrons be placed within the ring, a larger number can be maintained in equilibrium in one ring Thus a ring containing six electrons would not alone be stable, but if a seventh electron be placed within the hexoidal unstable ring, the system will become stable. A greater number of electrons will arrange themselves in a series of concentric rings Tables LXIII and LXIV illustrate the number of electrons arranged in a series of concentric rings which give systems in stable equilibrium when the number

of electrons in the system ranges from 1 to 67 These suffice to illustrate the principle involved

Mayer's Floating Magnets —The idea was neatly demonstrated by repeating an old experiment due to A M Mayer (1878–9). Small uniformly magnetized needles were thrust through discs of cork, and floated on water so that the negative poles of all the needles floated above the surface of the water while the positive poles were submerged These needles arrange themselves like J J Thomson's imaginary corpuscles when a positively charged magnetic pole is suspended a little above the surface of the water The diagram, Fig 324, shows that a group of four needles arrange themselves in the water at the four corners of a square, if another needle be thrown into the water, the five needles take up positions at the corners of a pentagon, if another needle be thrown in, five needles form a pentagon as before, but the sixth needle goes to the centre of the pentagon, if another needle be introduced, six arrange themselves at the corners of a hexagon, and the remaining needle goes to the centre Thus, a ring of six needles is unstable if hollow, but it is stable when another is placed inside This is an important principle in the formation of stable systems of negatively charged electrons It is obvious that *for stable equilibrium the structure must be substantial, a system with a large number of electrons on the outside, and none within, will be unstable*

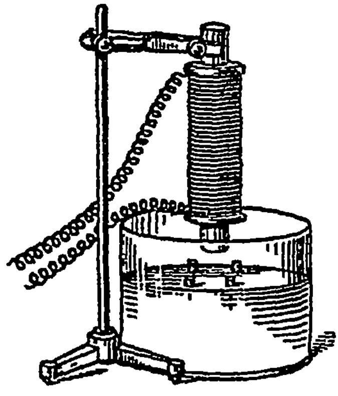


FIG 324 —Mayer's Floating Magnets

There is an important difference between Mayer's floating magnets, Thomson's systems of concentric rings of corpuscles, and the corpuscles in a real atom, because the two former are supposed to move in one plane (as on the surface of the water), whereas the corpuscles of an atom could no doubt move in any direction in space

The architecture of the atom —According to Lord Kelvin's hypothesis (1902) each atom is a remarkable constellation of electrons ranged in a system of concentric rings all assembled within a sphere of uniform positive electrification Although the mass of the negative electron seems to be $\frac{1}{1700}$ of that of the hydrogen atom, it cannot be assumed that the hydrogen atom contains about 1700 negative electrons, unless the mass of the positive electron be ignored The surface of the imaginary sphere may be regarded as the limiting surface of the atom The electrons are further assumed to be in rapid orbital motion about the centre of the sphere, and they are therefore driven outwards by a definite centrifugal force They are subject to the mutual repulsion of the negative electrons and the attraction of the total positive charge Positive electricity never appears apart from matter so that it is always associated with the atom itself. Some very interesting investigations have recently been made on the nature of the positive electrons In order to explain spectral phenomena, Nagaoka (1904) assumed that the positive charge is concentrated at a point in the centre of the atom, and the charge is not then uniformly distributed over the sphere As H Poincare expressed the idea "The

neutral atom may be considered to be composed of an immovable principle portion positively charged round which move, like satellites round a planet, several negative electrons of very inferior mass" Fig 325 gives but a crude notion of what is meant by concentric rings of corpuscles in rapid orbital motion about a central positively charged electron The atom has thus been compared with the planet Saturn and its rings This intricate mechanism is supposed to represent the inner structure of the chemist's *atom* The *atoms, in turn*, are supposed to be disposed in the molecule in an analogous manner Consequently, the relation of the electrons to the whole molecule must be somewhat complex The apparent hardness and impenetrability of the atom, so well emphasized by Newton, p 33, now appears to be a kind of gyrostatic equilibrium due to the rapidity of motion of the component electrons. We are told that a soft wax candle fired from a gun can be shot through a deal board, and that the speed of the jets of water in hydraulic mining in California was so great that a man could not strike an axe into the water which had just left the nozzle It is quite possible therefore that an atom may appear to be rigid owing to the rapid motion of the constituent electrons "Hardness," it is said, "is merely softness in rapid motion"

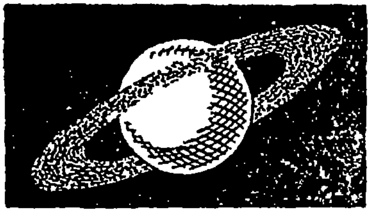


FIG 325 —Diagrammatic Representation of one form of the Corpuscular Ring Hypothesis of the Constitution of an Atom

The Saturnian atom —One reason for postulating the Saturnian atom as a basis for investigation is rather interesting J Plateau spun little spheres of oil in a mixture of alcohol and water so that they rotated while suspended in the liquid During their rotation the little spheres flattened at their poles and bulged at their equators When the speed of rotation of a sphere is great enough, rings of oil were thrown off The rings broke and coalesced to form little spherules which rotated on their own axes and revolved round the parent sphere This remarkable experiment has been used for illustrating a possible mode of formation of a solar system like ours from a contracting spinning nebula The Saturnian atom is supposed to be the figure of equilibrium of a mass of rotating electrons in a sphere of positive electrification It is not difficult to understand how the "figure of equilibrium" of a rotating fluid cannot be spherical, for gravity is progressively neutralized in passing from the axes of rotation (the poles) towards the equator, where the mass is specifically lighter The faster the spin the more oblate the spheroid, and in the extreme case with an increasing speed of gyration, the spheroid must become either a flattened disc, or else, at some critical velocity, there must be an interruption in the process of flattening, and the spheroid must alter fundamentally in shape or break into pieces H Poincaré (1885), G H Darwin (1879-81), and J H Jeans (1904) have investigated the subject mathematically

Rutherford's atom —In order to explain the scattering of the α rays by matter, E Rutherford (1911) assumed that the atom contains (i) a massive nucleus no larger than 10^{-12} cm in diameter and charged with positive electricity (ii) A cluster of negative electrons revolving about the central mucleus in orbital motion (iii) An outer group containing but a few electrons rotating about the inner group and which are much less rigidly attached to the atom To explain why the physical and chemical properties of the atom do not go hand in hand with X ray and γ ray phenomena, it is further assumed that (a) the outer group of electrons are

responsible for the physical and chemical properties of the atom, that (b) the inner group determines the phenomena associated with radioactivity, and that (c) the positive nucleus mainly determines the mass of the atom, while the groups of negative electrons are but a small multiple of the atomic weight Hence, the inner group can be called fixed electrons; and the outer group, valency or mobile electrons N Bohr (1913) has applied the quantum theory of radiation (p 573) to Rutherford's model atom to calculate the size of the atom, and he explains the series of lines found in the spectrum of some elements. The results deduced from the mathematical theory based on Rutherford's atom have been very encouraging

J W Nicholson (1914) has extended Bohr's work He calculated the possible spectral lines of nebulium, and found that his theory did not account for two of the lines which had been recorded for this element in the spectra of the nebulæ Wolf of Heidelberg later found that these two lines in the spectrum of the ring nebula in Lyra had a different origin from the true nebulium lines, Nicholson also predicted the existence of a new nebulium line not previously noticed, which Wright of the Lick Observatory found on photographic plates taken years previously, but which was so faint that it escaped notice

The periodic law —Ever since J B Dumas (1851) wrote

Every chemical compound forms a complete whole Its chemical nature depends primarily on the arrangement and number of the constituent atoms, and to a less degree on their chemical nature,

it has been considered a fundamental principle in chemistry that substances similarly constituted have similar properties If stable aggregates of electrons are similarly constituted, their properties, within certain limitations, will be similar even though the atomic weights be different An examination of the list of stable systems of electrons in Tables LXIII and LXIV, arranged in the order of increasing mass, shows that there is a certain similarity in the grouping at certain intervals Thus, the properties connected with a five ring group can only recur at intervals, similarly with the properties of the "doublet" 10- and 5-ring group, the triplet 15-, 10-, and 5-rings, and the quartet 17-, 15, 10-, 5-rings Hence, we can divide the various groups of electrons into families such that any one family is derived from the preceding members by the addition of another ring of corpuscles. Thus

Number of corpuscles in successive rings	21	17	15	10	5
	17	15	10	5	–
	15	10	5	–	–
	10	5	–	–	–
	5	–	–	–	–
Total number of corpuscles	68	47	30	15	5

This idea gives a rather definite conception of the meaning of the periodic law A periodic law thus appears as a necessary consequence of the hypothesis that atoms are built of stable systems of concentric rings of electrons, for obviously, *certain rings of electrons recur periodically with an increase in the number of electrons which make up the atom*, and atoms with related rings must possess many common properties in virtue of the similarity in the grouping of some of the rings Thus, J J Thomson has demonstrated that the spectra of such groups would be in many ways similar

The misfits in Mendeléeff's table—It is even possible to see how elements with similar properties may fall into the "wrong" group in Mendeléeff's table if classed solely by their atomic weights Starting from sodium in the scheme on p 808, we can see that if the elements are really formed by the aggregation or condensation of electrons (p 830), the sodium atom might collect more electrons until, say, two different stable systems capable of separate existence are formed Thus, sodium might furnish two subgroups—potassium and copper The properties of an element are supposed to be determined by the structure of rings of electrons, and differences in the properties of members of the subgroups is due to the differences in the internal structure of the atoms although the atoms probably possess some rings in common Each subgroup, by a further condensation of electrons, forms the succeeding family members indicated in the vertical columns of the table Consequently, it is quite true, in a general way, to say that the elements were evolved in the order of their atomic weights, but they must also have evolved in groups down the vertical as well as along the horizontal lines Hence, as J N Lockyer observed (p 823), the elements do not always appear in the cooling stars in the order of their atomic weights In virtue of this multiple growth hypothesis of A C and A E Jessup (1908), it is to be expected that in some cases an element in any particular group may contain more or less electrons, and hence have a slightly greater or less atomic weight than adjacent elements in the next succeeding group

Working from an atom of the Rutherford type, J W Nicholson (1914) has calculated spectral lines for vibrating electrons in systems with an assumed atomic number 1e, 2e, 3e, 4e 5e and 6e corresponding with Moseley's atomic number, and with the respective atomic weights

Element	Prh	—	—	Nu	Pf	Arc
Atomic number	1e	2e	3e	4e	5e	6e
Atomic weight	0 082	0 327	0 736	1 31	2 1	2 9

The lines corresponding with 1e exist in the spectra of nebulæ and have been assumed to belong to an unknown primitive element called *proto hydrogen* Prh, the lines corresponding with 2e are present in nebulæ and in Nova Persei similarly faint lines corresponding with those computed for 3e are found in nebulæ 4e belongs to *nebulium*, Nu the lines for 5e have not been found in nebulæ, but those in the solar corona have been supposed to represent a non terrestrial *proto fluorine*, Pf, the lines for 6e exist in the spectra of nebulæ and have been supposed to represent an unknown element *arconium*, Arc Lines corresponding with 7e are also found in nebulæ

Electronegative and electropositive characters—Some of these systems are more stable than others Consider the properties of the systems with 20 rings on the outside—Table LXIV The first member with 59 electrons is on the verge of instability, and when it is subjected to a small disturbance, a negative electron can be readily detached from the outer ring If one negative electron were lost from it, the residue would have a positive charge, and it would behave like a positively charged ion, that is like an electropositive or basic element The system with 60 electrons is more stable than the one with 59, and it will not be so readily broken as the preceding This means that this system will not be so basic as the preceding Similarly the system with 61 electrons will be less basic than the one with 60, and 62 will be less basic again than 61. In 63,

the stability is so great that there is little danger of losing electrons from the outer ring, and an electron could lie on the surface of the system without breaking a ring In that case, the system would receive a negative charge and behave like an electronegative or acidic element. Hence, the electronegative elements may be regarded as possessing neutral atoms with a tendency to absorb negative electrons from without, and electropositive elements are regarded as neutral atoms with a tendency to part with negative electrons The electronegative character increases with increasing atomic weight until the system with 67 electrons is reached. This corresponds with the fact that in Mendeleeff's list of elements the electronegative property is practically zero at the end with the alkali metals, and gradually becomes more marked with increasing atomic weight until, at the halogen end, it attains its maximum value The system with 68 electrons resembles 59 in respect to stability, etc, and 69 resembles 60, and so on

TABLE LXIV

Total number of electrons	Number of electrons in succession rings (numbered onwards)				
	1	2	3	4	5
59	20	16	13	8	2
60	20	16	13	8	3
61	20	16	13	9	3
62	20	17	13	9	3
63	20	17	13	10	3
64	20	17	13	10	4
65	20	17	14	10	4
66	20	17	14	10	5
67	20	17	15	10	5
.					

Null-valency —The system with 58 electrons is very stable and consequently, as soon as the 59-system has lost one electron, no more can escape because the system which remains is the most stable of all the systems with 19 electrons in the outer ring The positively charged residue will therefore attract surrounding electrons so that one will immediately dart back to it, and reform the system with 59 electrons The system so formed will break up as before and the same cycle of changes would be repeated over and over again Hence the 59 system will not remain permanently charged. directly it loses an electron another takes its place. Such an atom would be unable to retain a positive or negative charge permanently, and it would not be able to enter into chemical combination Consequently, it would behave like the members of the group of inert gases

Valency —The system of 60 electrons will be the most electropositive of the series.

59, 60, 61, 62, 63, 64, 65, 66, 67

with 20 electrons in the outer ring It can lose but one corpuscle because, if it lost two, the residue with 58 electrons would behave as if one electron from the group 59 had been removed, and, as we have seen, the 58 system would immediately attract an electron Hence, the 60 system can lose one electron and form a system carrying unit charge of positive electricity This means that the 60-system is univalent The system 61 would not be so ready to part with electrons as 60, but it could afford to lose two electrons since it is not reduced to the 58 group until it has lost three electrons The group with 61 electrons must therefore be bivalent

Against this, however, it must be remembered that positive ray analysis shows that there is no relation between the number of electrons an atom can lose and the valency of the element, thus the inert gas helium readily loses two electrons, the argon atom can carry 1, 2, or 3 positive charges, krypton, four, etc

Chemical combination—Suppose that we have an atom of the type 60, and one of the type 67, the former would be illustrated by an atom of sodium, and the latter by an atom of chlorine, the former can *lose* one negative electron, and the latter can *gain* one, but not more than one The electrons which escape from the sodium atom can find a home on the chlorine atom, and if an equivalent number of both be present, each of the sodium atoms will acquire a positive charge, and each of the chlorine atoms a negative charge The oppositely electrified atoms will attract one another, and form a compound NaCl. When electropositive and electronegative atoms are brought into proximity, the former loses and the latter gains an electron, as a result, the former acquires a positive and the latter a negative charge, and the force of chemical affinity is the attraction exerted by the electropositive atom for the electron it has lost to the electronegative atom Similarly, if equivalent quantities of atoms of the type 61 and 67 had been mixed, and this would be illustrated by calcium and chlorine atoms, the atoms of calcium would each lose two negative charges, and each of the chlorine atoms would gain one negative charge Thus a neutral system would be formed by the combination of two chlorine atoms with one calcium atom, and $CaCl_2$ would result Hence, says Thomson, from this point of view a univalent electropositive atom is one which can lose one and only one electron to form a stable system under conditions which prevail when chemical combination is taking place Similarly, *mutatis mutandis*, with univalent electronegative atoms, bivalent atoms, etc Thus, the affinity of an atom depends upon the ease with which an electron can escape from or be received by the atom This may be influenced by the conditions prevailing at the time chemical combination is taking place If the atoms be diffused in a good conducting medium it would be easier for a liberated corpuscle to resist being pulled back to the original atom than if the atoms were diffused in a non conducting medium Hence the valency of an atom may be influenced by the physical conditions under which it is placed The ability of an atom to enter into chemical combination depends upon its power of acquiring a charge of electricity Thus chemical affinity is electrical affinity, or, as H Davy expressed it in 1810, "electrical and chemical attractions are produced by the same cause acting in one case on particles, and in the other on masses"

Abegg's normal and contra valencies—We have just seen that the 60 system can acquire one and only one positive charge by the loss of one negative electron, but it is conceivable that additional negative electrons could be forced into the system so that the total number of electrons increase to 61, 62, 63, 64, 65, 66, and 67, and at the same time the systems would become more and more stable If an additional electron were forced into the 67 system, an unstable system with 68 electrons would be formed Consequently, 67 is the greatest number of negative electrons which we can hope to force into the 60 system to furnish a stable system with an electronegative valency of 7—the electropositive valency of the

60 system is one Similarly, *mutatis mutandis*, with the other systems, and Thomson has tabulated the properties of the systems containing 59 to 67 electrons as follows

Number of electrons	59	60	61	62	63	64	65	66	67
Valency	+0	+1	+2	+3	+4	−3	−2	−1	−0
	−8	−7	−6	−5	−4	+5	+6	+7	+8
	Electropositive					Electronegative			

This sequence of properties imitates that observed with the elements·

He, Li, Be, B, C, N, O, F, Ne
Ne, Na, Mg, Al, Si, P, S, Cl, A

The first and last members of the series only are null-valent, the second set is univalent electropositive, and the last but one univalent electronegative, the third is bivalent electropositive, and the last but two bivalent electronegative, etc

This recalls an observation of D I. Mendeléeff to the effect that the sum of the maximum oxygen and hydrogen valencies of the elements in certain groups of the periodic series is equal to 8, *e.g*,

SiH_4, PH_3, SH_2, ClH
SiO_2, P_2O_5, SO_3, Cl_2O_7

In ignorance of the number of electrons in successive rings, it is inferred that the number of mobile electrons in the outer ring cannot exceed eight, and this represents the greatest charge which has yet been observed, the minimum is zero It is further assumed that there is a tendency for these electrons in every atom to assume either the maximum or the minimum value Thus, if an atom has five mobile electrons, it can either lose all five and acquire a positive valency of five, or it can attract three more electrons from without, make its complement up to eight, and thus acquire a negative valency of three Which of these two possible effects will take place, will depend upon the nature of the neighbouring atom Thus, if a phosphorus atom be surrounded by hydrogen atoms, under the right conditions of temperature, etc, its behaviour would correspond with its gaining three electrons, becoming electronegative, and forming PH_3 with a maximum valency of three, on the other hand, if it be in contact with a strongly electronegative element like chlorine, it appears to lose five electrons, become electropositive, and to form PCl_3 or PCl_5 with a maximum valency of five Variable valency here meets a rational interpretation, for the whole of the available electrons need not be always removed together The work done in removing a second electron must be greater than is involved in removing the first So with phosphorus, the force exerted by the electronegative chlorine atom may suffice to drag three electrons from the phosphorus atom, but only when the conditions are favourable is it possible to drag off another two This does not explain the rarity of intermediate valencies between three and five

From purely chemical considerations, too, R Abegg (1902–4) was led to assume that every element possesses a maximum valency of 8 made up of positive and negative components according as the element is acting as an electropositive or electronegative constituent of a compound. The two valencies of opposite polarity are called normal valencies and contra

valencies The normal valencies are supposed to be the stronger, and correspond with the usually accepted maximum valencies of the elements In the case of the metals the normal valencies are positive and the contra valencies negative, while in the case of the non-metals, the normal valencies are negative, and the contra valencies positive Thus

	Na	Mg	Al	Si	P	S	Cl
Normal valencies	+1	+2	+3	+4	−3	−2	−1
Contra valencies	−7	−6	−5	−4	+5	+6	+7

Thus, chlorine is univalent in HCl where it is combined with electropositive hydrogen, but it has its maximum heptavalency when united with electronegative oxygen in chlorine heptoxide A Werner has also shown how elements have a different valency according as they are united with electropositive or electronegative elements The relative strengths of the two kinds of valency depend upon the nature of the associated atoms The alkali metals are so strongly electropositive that they show little if any sign of an electronegative valency, and fluorine appears to be too strongly electronegative to show a positive valency, for it forms no compound with oxygen When the conditions are such that the latent contra valencies become operative, complex "molecular" compounds may be formed

The fact that in a given family the elements with the greatest atomic volume are usually most electropositive and least electronegative, is taken to mean that when two atoms of different sizes are in contact, the attraction of the smaller atom for the corpuscles in the larger atom is greater than the attraction of the larger atom for the corpuscles in the smaller, so that the resultant force will drag corpuscles from the larger to the smaller atom Again, since the atomic volume increases with the atomic weight, the electropositive character of the elements in a given family increases with the atomic weight Examples have been indicated in reviewing the different family groups of elements

Radioactivity—According to J J Thomson's hypothesis, atoms are built of systems of rotating rings of electrons The configuration of a system of rotating rings of electrons is dependent not only upon the number, but also upon the energy of the speed of rotation of the rings. Four electrons, for instance, may arrange themselves at the corners of a square or a tetrahedron If a four square system of electrons be rotating faster than a certain critical value, they will be stable, but if their velocity falls below the critical value, the arrangement will become unstable, and the electrons will suddenly arrange themselves in the form of a tetrahedron Similarly, if a spinning top be rotating faster than its critical value, it will remain stable in a vertical position, but if the speed of rotation falls below this value, the top becomes unstable, and falls down, in doing so, it gives up a considerable amount of energy These analogies can be extended to complex groups of electrons, say a radium atom Owing to the radiation of energy, the kinetic energy of the electrons is gradually reduced, and the velocity of the spinning rings of electrons must be slowly diminishing When the velocity approaches the critical value, the configuration of the system may be modified, and this is accompanied by an increase in the rate at which kinetic energy is lost by the radiation When the velocity reaches the critical value, the configuration becomes unstable

an atomic cataclysm, or an atomic explosion occurs, and a number of electrons are detached from the original assemblage In other words, the atom disintegrates and a part of the atom is shot off to form two or more groups of electrons This corresponds with the emission of α-rays and emanation from radium As G H Darwin (1905) expressed it, the laws of electricity in motion proves that a community of electrons, as pictured by Thomson, must be radiating or losing energy, and therefore the time must come when it will be run down as a clock does The aggregate will then spontaneously change into another system (or element) which needs less energy than was required in the former state If the atoms of the emanation are built of electrons of the same type as the original atom, the process may be repeated with the sub-atoms, and so produce a series of degradation products with a long or a short life This shows that with atoms of a special kind—*e g* high atomic weights—the gradual reduction of the kinetic energy of the electronic motion might produce instability within the atom The rate of decrease of the kinetic energy may take thousands of years before it reaches its critical value, or it may take place in a very short time The atoms of the several elements thus represent different aggregates of electrons which have proved by their stability to be successful in the struggle of the elements for a separate existence

An enthusiastic writer declares that " the corpuscular theory of Thomson has enabled chemists to explain the periodic law, valency, chemical action, etc , in terms of known facts " We are also told that more is known about the atom than about matter *en masse* These are surely based on superficial views which are the result of confusing fact and fancy The electronic model atom has but a remote analogy with the real atom Analogy may be an invaluable aid to description, but it cannot *prove* a single fact Thomson quite recognized the inadequacy of his model atom, for he points out that the number of electrons corresponding with a particular property will doubtless be different if the electrons are distributed in three-dimensional space instead of in concentric rings But since similar properties are associated with rings as with shells, it is probable that a system of concentric shells will present somewhat analogous properties A more complex disposition of the electrons will obtain if the positive electrification be not uniformly distributed in the sphere as indicated above Hence, with all its imperfections, Thomson's hypothesis throws a most interesting light on Mendeléeff's series and on the possible nature of an atom; though matter still remains an inscrutable and impenetrable mystery—but we are still puzzled, for, as W Crookes (1886) has said "The list of elements extends before us as stretched the wide Atlantic before the gaze of Columbus, mocking, taunting, and murmuring strange riddles which no man has yet been able to solve " Each forward step in our knowledge carries us backwards to a vaguer and remoter past

Perhaps the most interesting point about the hypothesis is the fact that the valency and the properties of the members of Thomson's series vary periodically with a gradual increase in the number of the constituent electrons, that is, with the atomic weights, but an examination of Tables LXIII and LXIV will show that the variation is not like Mendeléeff's series The fact that the series with 20 electrons in the outer ring corresponds with seven elements in Mendeléeff's even series is rather

due to chance, because the number of elements with 19 corpuscles in the outer ring is 4; with 20 in the outer ring, 9; and 10 with 21 in the outer ring. In S. Arrhenius' words (1907): "the number of elements belonging to a Thomson's series will increase nearly proportionally to the two-third power of the atomic weight of its first element; therefore the number of elements in the seventh series ought to be about three times as great as that in the third series, and about eight times as great as that in the second series."

§ 14 Electronic Hypotheses of Chemical Combination and Valency

Truth is the daughter of time.—FRANCIS BACON.

In recent years there has been a constantly growing tendency to apply the electronic theory to explain chemical phenomena. It is assumed that electricity has an atomic structure (p. 305), and is not continuous; and that positive and negative units of electricity are associated as constituent parts of the chemical atom. Consequently, the association of atoms to form molecules involves an investigation of the structure of fields of force exerted on the outer surface of the atom. The different hypotheses usually take one of two forms:

1. Every chemical bond between two atoms involves a *transfer* of one negative electron from one atom to the other, so that the one atom is charged positively and the other negatively—*vide* p. 306.

2. If the electrons are actually displaced, J. Stark (1908) considers that some phenomenon resembling the selective absorption of light takes place, and that when the electrons return to the atom a phenomenon resembling fluorescent radiation occurs.

(*a*) In one form of Stark's hypothesis (1908) the units of positive electricity are supposed to be situated on the surface of the atoms, not as uniformly charged zones, but rather concentrated at certain points, and the neutralizing electrons are assigned definite positions on the surfaces of the atoms. The negative electrons hold the positive atoms each to each, as illustrated diagrammatically in Fig. 326, where the dotted lines represent tubes or lines of force.

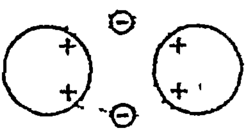


FIG. 326

(*b*) In J. J. Thomson's hypothesis (1914), the electric forces which keep the atoms together originate in a *displacement* of the positive and negative electricity in each atom; and as a result, each atom acts like an electric doublet and attracts another atom, much in the same way that two magnets attract one another.

J. J. Thomson's theory starts from the assumption that an atom is an aggregate of negative electrons with a sphere of positive electrification. The charges may or may not counterbalance one another, leaving the atom either electrically neutral or polarized, that is, charged with a surplus of positive or negative electricity. A pair of balanced charges is called an electric doublet, and W. Sutherland suggested the hypothesis that the peculiar force exerted by an atom is the same as if each atom carried an electric doublet whose moment is characteristic of the atom. Sutherland's atoms therefore characterize compounds of the first class, but not the second

The field of electric force about the molecules of a compound — From the known properties of electrified bodies, it is inferred that a field of electric force must envelop each atom no matter whether the opposite charges wholly or partially counterbalance one another Even an electrically neutral atom will have a field of force which (i) will not be uniformly distributed about the atom, and which (ii) will probably diminish in intensity more rapidly than the inverse square of the distance The field of force emanating from the charges in the atom will give rise to (*a*) *intramolecular attractions* whereby the charged atom affects the other atoms associated with it in the molecule, but it will also give rise to (*b*) *intermolecular attractions* because the field of force of an atom will also attract the atoms in other molecules, and so produce phenomena like the surface tension of liquids, latent heat of evaporation, cohesion of liquids and solids, etc Accordingly, chemical compounds can be divided into two classes

I *Molecules with uncharged or neutral atoms* —The individual atoms of the molecule are neutral, for the constituent atoms are charged with equal amounts of positive and negative electricity, and there is no surplus or excess of the one kind over the other *E g* H_2, O_2, He, N_2, Cl_2, CO, CO_2, CS_2, CCl_4, C_6H_6, N_2O, etc

II. *Polarized molecules, or molecules with charged atoms* —The individual atoms within the molecules carry an excess of positive or negative electricity so that the whole molecule is charged, and, accordingly, exerts larger forces upon the atoms of neighbouring molecules than would be the case if the atoms were neutral. The chemical reactivity, specific inductive capacity, surface tension, cohesion, tendency to form molecular complexes, and other qualities of such compounds are found to be highly developed *E g* H_2O, NH_3, HCy, SO_2, HCl, CH_3OH, C_2H_5OH, CH_3Cl, etc

The distribution of the electric charges within the molecule — Each element has its own specific attraction for negative charges, thus, sodium exerts a less attraction for negative charges than chlorine, otherwise expressed, sodium is more electropositive than chlorine With carbon monoxide, although the opposite charges on the two atoms neutralize one another, yet the oxygen has a greater attraction than carbon for a negative charge Hence, a certain amount of work is available in the transfer of a negative charge from the atom in which the attraction is weak to an atom in which the attraction for the negative charge is strong Accordingly, when a neutral electropositive atom is united with an electronegative atom, the negative charge tries to pass from the former to the latter and electrify it negatively Why does not the transfer always take place ? Thomson assumes that electricity has an atomic structure, and must pass in definite units from one point to another, and therefore a whole charge must be transferred or none at all He illustrates the action by diagram, Fig 327 Each atom C and O carries a balanced positive and negative charge. The O is more electropositive than the C, and there is therefore a tendency for a negative charge to pass from the C to the O atom, but this tendency does not suffice to overcome the attraction of the positive charge carried by the C atom This latter is diminished by bringing up another atom represented by the dotted line, Fig 328 This helps the passage of the negative charge across to the O atom Thus, the atoms of a compound may be uncharged when isolated, and yet become charged

when the compound is in a liquid state, or when the atoms are combined to form more complex molecules The term intramolecular ionization,

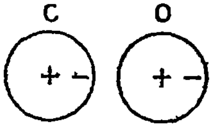


FIG 327 —Carbon monoxide, CO, with neutral atoms

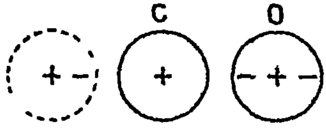


FIG 328 —The charging of a carbonyl, CO, radicle

by the way, is applied by J J Thomson to the process by which the atoms of a molecule get charged electrically

Leyden jar analogy —J J Thomson compares the two atoms of, say, carbon monoxide with the two coatings of a Leyden jar so that the whole molecule behaves as if it were a Leyden jar of small capacity It is known that the smaller the capacity of a jar, the greater the amount of energy required to transfer, say, *q* units of electricity into the jar If the available energy be less than this, the transfer of, say, a single negative charge from a carbon to an oxygen atom will not occur, and *vice versâ* By increasing the capacity of the "jar," a transfer might occur which would otherwise be impossible Hence if another molecule be added to a certain atomic system its capacity might be increased and accordingly less work might be required to transfer a charge from an electropositive to an electronegative atom

Platinum tetrachlorodiammine, $PtCl_4(NH_3)_2$, is not an electrolyte, because its atoms are electrically neutral Add another molecule of ammonia to get $PtCl_4(NH_3)_3$, and the resulting compound is an electrolyte with a molecular conductivity of 97, this number rises to 228 with the addition of another molecule of ammonia to form $PtCl_4(NH_3)_4$, and up to 553 when two more molecules of ammonia are added to form $PtCl_4(NH_3)_6$ Thus, as the molecules of ammonia are increased, the charges carried by the atoms increase rapidly Carbon monoxide is neutral, but when it enters as a carbonyl radicle into organic compounds—like acetone $(CH_3)_2CO$, aldehyde, CH_3COH, etc —it raises their specific inductive capacity because the CO radicle becomes charged on entering the compound The proximity of other atoms increases the capacity of the system sufficient to allow the transfer in question Mere contact with the other atoms promotes intramolecular ionization In some cases, some of the radicles or atoms may carry one or more charges, and other atoms may be electrically neutral. The hydroxyl radicle, OH, may exist in a molecule in two states according as the oxygen atom carries one or two negative charges If the oxygen atom carries one charge, the radicle $O^-—H^+$ will form an electric doublet, and if two charges—as is probably the case with water—there must be a positive charge on some other radicle not the hydroxyl group, and there will be two doublets in the molecule J J Thomson suggests that the difference in these two states determines whether the OH radicle acts as an acid or as a base Acidic hydroxyl is represented by $O^-—H^+$, and basic hydroxyl (of water) $O^=—H^+$, for if the molecule $RO^-—H^+$ be in solution and surrounded by H^+ and $O^=—H^+$ ions, arising from the dissociation of water, the H^+ ion of the given molecule would unite with the $O^=—H^+$ of the water, and leave an excess of H^+ ions in solution so that the molecule $RO^-—H^+$ would have acidic properties, on the other hand,

in the molecule $R^+—O^=—H^+$, the $O^=—H^+$ of the molecule would unite with the H^+ from the dissociation of the water and leave an excess of $O^=—H^+$ ions in the water, and the molecule would have basic properties. The more electropositive the element R in the ROH molecule, the more likely is a corpuscle to be transferred from the R to the O atom, and accordingly the more likely is the oxygen to acquire a second charge and show basic properties.

Valency electrons or corpuscles.—J. J. Thomson (1914) further suggests that each atom may contain negative electrons related to the atom in two ways. (i) *Fixed electrons.* Some of the electrons are firmly fixed at the core of the atom; they are not free to adjust themselves so as to cause the atom to attract other atoms into its neighbourhood; and they take no part in chemical reactions. (ii) *Mobile or valency electrons.* Some of the negative electrons are supposed to be located near the surface of the atom, and they are free to move about and set themselves into position under the influence of external electrical fields. They are linked with the central positive charge of the atom by lines of force. The mobile electrons, which J. Stark (1908) called *Valenzelectronen*, enable the atoms to hold on to one another and form a bond between joined atoms. The number of mobile corpuscles determines the valency of the atom so that a univalent atom has one, a bivalent atom, two, and a septivalent atom has seven mobile

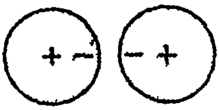


Fig. 329.—Repulsion.

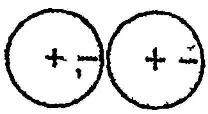


Fig. 330.—Attraction.

electrons. The mobility of the electrons is an essential condition necessary for one atom to exert any considerable attraction on another. For example, if an atom with one mobile negative electron—Fig. 329—and another atom with its negative electron—Fig. 330—were in contact, the two atoms would attract or repel one another as illustrated in the diagrams. If, however, the electrons are free to move, they will be driven apart until the positive charge of the one atom is nearer to the negative charge of the other, and the atoms would then attract one another. The negative corpuscle has very little inertia and, if free, can be driven round at once. The initial repulsion would therefore be momentary and attraction would be the final result. If the corpuscle was fixed, it could not swing round without carrying the whole atom, which is a comparatively heavy body difficult to move. As a result, when the corpuscles are mobile, the atoms are kept together, but when the electrons are fixed, the atoms will have comparatively little attraction for one another. When the negative corpuscles of the atom are so firmly fixed as to be incapable of exerting any great attraction on other atoms surrounding it unless they are in particular positions, the valency of the atom is said to be saturated, for the satisfaction of a valency is essentially the fixing of one of the mobile negative particles.

Fixing the valency electrons.—Assume that each negative electron in an atom is the origin of a line or tube of force. If the atom is alone, the

line of force will return to the same atom and end on its own positive charge as illustrated diagrammatically, Fig 331 The negative electron is still free to move Consequently, an electron will not be fixed when the atom is by itself, but only when the line of force from the corpuscle is anchored to an opposite charge on another atom *B*, Fig 333 The electron is then deprived of its mobility, and is unable to attract another atom

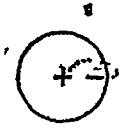


Fig 331 — Tube of Force of a Mobile Corpuscle

Case I If the two atoms be electrically neutral, a similar tube of force will pass from each negative electron on each atom to the positive charge on the other atom, as illustrated diagrammatically (Fig 333) Hence, with neutral atoms, for each tube of force which leaves an atom there will be a return tube—as many will go out as come in If the atoms are each bivalent, two tubes of force will leave each atom and two return , in general, in compounds with neutral atoms the total number of lines of force between the constituent atoms is double the chemical valency This means that J J Thomson would represent each chemical valency by *two* bonds between the atoms of a molecule when the constituent atoms are electrically neutral. It does not follow that if the atom A sends a tube of force to another atom B, it must receive one from the *same* atom B, for the return tube may come from *another* atom The necessary condition is that the number of tubes of force which leave an atom must be equal to the number which return With this understanding, certain combinations can be explained which appear to be anomalous in the light of the old valency hypothesis If hydrogen be univalent, a combination like H_3 was considered impossible on the older hypothesis But the hydrogen molecule has neutral atoms, with two tubes of force issuing from each The molecule H_3, that is—

H
H△H

is thus quite compatible with the hypothesis, so also is a molecule H_n Again, with monatomic silver AgCl, $AgCl_2$, $AgCl_3$, and $AgCl_n$ are all possible valency compounds in this extension of the older valency hypothesis. The trouble with the hypothesis is that it apparently explains too much

Case II If the two atoms be charged electrically —We have seen that an electron will be fixed when its tube of force passes out of its atom and ends

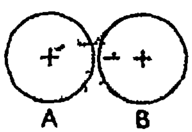


Fig 332 —Union of charged atoms.

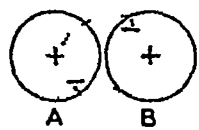


Fig 333 —Union of neutral atoms

upon some other atom, Fig 333 If one of the negative electrons (Fig 332) be dragged from one atom, A, to the atom B, the electron would follow its tube of force which left the atom A, and the tube of force would shrink up in the atom B, and only one tube of force would connect the two atoms.

When a number of electrons are transferred from one atom to another, the number of tubes of force between the two atoms will be halved, because after the transfer no tube of force will leave the electropositive atom, and none will enter the electronegative atom The one atom, B, would thus be positively charged and the other, A, negatively charged Hence, in compounds with charged atoms, the number of tubes of force between the constituent atoms will be equal to the chemical valency The tube of force is then equivalent to the bond or bar of the regular structural formulæ (p 69) employed by chemists, and the valency bond is only applicable when the constituent atoms are charged electrically If the constituent atoms are electrically neutral each valency bond must be doubled if it is to represent a tube of force The chemist's hyphen or bond is thus related with the physicist's tube of force

Unsaturated compounds —It follows from the preceding discussion that when each of the mobile electrons in an atom is anchored by a tube of force to a neighbouring atom, the average attraction of that atom for other atoms is reduced to a minimum J J Thomson further shows that if the molecule of a compound is to exist in a stable form, (i) The molecules must not exert a sufficiently large attraction on the neighbouring atoms to cause them to unite and form other molecular systems This will be the case when the work required to separate the two molecules under consideration is small compared with the average kinetic energy of the molecule at the temperature T (ii) The attractions between the atoms of the molecules must be great enough to prevent a separation when the molecule collides with other molecules This will obtain if the work required to separate the atoms is large compared with the average kinetic energy of the molecule at the temperature T These conditions are greatly influenced by temperature Thus, with iodine vapour, the monatomic molecule may exist in a stable form at a high temperature, and pass into more complex diatomic molecules at lower temperatures

If carbon monoxide is a stable compound when electronegative carbon is united with the more electronegative element oxygen, why does not CCl_2 also form a stable compound? Thomson answers this question as follows As already indicated, an atom, even when saturated, must produce an electric field in its neighbourhood This field must restrict the freedom of motion of molecules of the corpuscles in neighbouring atoms If the electric field due to the oxygen atom in carbon monoxide be very strong, then, even though but two of the four mobile corpuscles of the carbon atom are bound to the oxygen by tubes of force, the other two will be exposed to so strong an electric field that their mobility is reduced As a result, the attraction of the carbon atom on other atoms is reduced The amount of residual attraction, so to speak, depends upon the strength of the electric field in the carbon atom produced by the oxygen atom If the electric field with the CCl_2 system be smaller than that produced in the CO system, it follows that the latter will behave more like a saturated molecule than the former, and the carbon monoxide molecule, in consequence, might exist in a free state when the CCl_2 could not

It might be argued that in a compound like ethane, C_2H_6, with electropositive hydrogen atoms, and electronegative carbon atoms, the two carbon atoms are in a different electrical state, because the tubes of force from three hydrogen atoms end on each carbon atom, and a tube of force from one

carbon atom must end on the other, accordingly, the potentials of the charges on the two carbon atoms must be different This is illustrated diagrammatically in Fig 334. Similar remarks apply to acetylene and probably also to ethylene linkages No phenomenon has yet been noticed which would justify this conclusion in the case of ethane, but in the case of doubly and triply linked combinations, several properties—molecular volumes, indices of refraction, etc —are markedly different from what they are with the carbon atoms all singly linked together

This discussion has not proved these speculations, it only makes them appear plausible The work outlined in this chapter illustrates the invaluable aid which chemistry and meta-chemistry are receiving from the disciplined imagination indicated in our preface Naturally many have fallen before the temptation to confuse imaginary phenomena with demonstrated fact Premature generalizations are rife, since, as a rule, the less the number of facts, the easier it is to generalize —and the more likely are those generalizations to be wrong

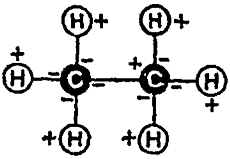


Fig 334 —Ethane, C_2H_6

The honesty of science—Here, then, we are confronted with phantasmæ which would be banished at once if we were convinced that they were sterile conjectures and not pregnant hypotheses The speculations probably make the best guess yet made about the ultimate constitution of matter The relations between hypotheses and fact, though doubtful, are not altogether contradictory Consequently, the defective hypotheses will be persistently attacked by hostile forces until they are either abandoned in favour of more successful rivals, or developed and strengthened into a more consistent and lasting form

This struggle for existence is the life and strength of scientific hypotheses Science may appear to lose influence when the fallacy of a prevailing hypothesis is demonstrated, but it holds a treasured reputation for honesty of purpose by frankly acknowledging and registering its mistakes In the words of A Sidgwick, free from the fear of being found an impostor, science is able to challenge—and to court—correction "As for the truth, it endureth, and is always strong, it liveth and conquereth for evermore Truth is the strength, the kingdom, the power, and the majesty of all ages"—1 Esdras iv

EPILOGUE

THERE are not far from 200,000 different compounds known to chemists, and hundreds of new compounds are discovered every year The specific properties of all these substances are described in dictionaries of chemistry, and in memoirs of the various scientific societies The student of chemistry is not expected to be acquainted with more than a small fraction of these compounds. If a chemist discovers what he believes to be a new compound, it is possible to find if it has been previously prepared by consulting the literature just mentioned.

Herbert Spencer has properly said that in so far as the production of new compounds is carried on merely for the sake of obtaining new compounds, chemistry is not a science, but an art The best chemist is not necessarily he who is familiar with the greatest number of compounds Chemistry is something more than a compilation of empirical facts Dictionaries of chemistry, not the memory, are the natural storehouses of isolated facts The intellect is perfected not by knowledge but by exercise The time needed for memorizing a vast medley of facts can be far more profitably spent in training the brain to think clearly and logically, and the hands to do their work skilfully and accurately. A student trusts his teacher to equip him with these essentials, and the conscientious teacher has therefore grave responsibilities. At the same time, the work of the teacher may be reinforced or hampered by an examination syllabus which the student expects to traverse

The experience of thousands of teachers crystallized in hundreds of text-books, syllabuses of examinations, etc, is supposed to have taught teachers what facts and principles the student of general chemistry should know But the teacher has failed in his work if he has not whet the student's appetite for more The subsequent progress of the student in general chemistry is, however, largely determined by his intended profession, and I question if hereafter he can do better than follow the advice of "Sherlock Holmes"

I consider that a man's brain originally is like a little empty attic, and you have to stock it with such furniture as you choose A fool takes in all the lumber of every sort that he comes across, so that the knowledge which might be useful to him gets crowded out, or at best is jumbled up with a lot of other things so that he has a difficulty in laying his hands upon it Now the skilful workman is very careful indeed as to what he takes into his brain attic He will have nothing but the tools which may help him in doing his work, but of these he has a large assortment, and all in the most perfect order It is a mistake to think that this little room has elastic walls and can distend to any extent Depend upon it there comes a time when for every addition of knowledge you forget something that you knew before It is of the highest importance, therefore, not to have useless facts elbowing out the useful ones

MISCELLANEOUS QUESTIONS

1 What is meant by (*a*) chemical action, and (*b*) physical change? Is chemical action always accompanied by physical change? In the following list of changes, which are chemical? and which of a physical nature?—Souring of milk, digestion of food, liquefaction of air, freezing and evaporation of water, grinding of grain, fading of coloured fabrics, withering of leaves, weathering of rocks, melting of silver, solution of sugar in water?—*Princetown Univ* (*U S A*)

2 Discuss the following quotation "The volume of a molecule of a compound body in the gaseous state is exactly double the atom of hydrogen"

3 What were the principal difficulties in the way of the general acceptance of the atomic theory as enunciated by Dalton? Show how these difficulties were overcome —*Sydney Univ*

4. Suppose the mineral chromite on analysis furnished the equivalent of 50 per cent Cr_2O_3, on the assumption that the atomic weight of chromium is 52 1 (O=16) What difference in the value of a ton of chromite will be reported by two chemists if one works on the assumption that chromium has an atomic weight of 51 6 and the other 53 5? Given a 50 per cent ore is worth £3 5s 0*d* per ton

5 In reply to the question 'State the laws of constant composition, give an example," a candidate up for examination answered "Chemical combination always takes place between different masses of matter, *e g* two of hydrogen to one of oxygen" Is this answer worth any marks? Why?

6 Criticise the following extract from the paper of a candidate for examination "Gases unite chemically by measure as well as by weight, solids and liquids unite only by weight"

7 Suppose it be argued that in the experiment depicted in Fig 12, the moisture might come (*a*) from the air, or (*b*) from the imperfect drying of the hydrogen gas, how would you proceed to modify the experiment to test if these objections stultify the inference drawn?

8 Explain the following quotation 'A fact which will not fit into reasoned and formularized schemes stands outside scientific knowledge until the right formula is found"—*J J Murphy* (1869)

9 What did T Bergmann mean when he said that "the qualities of bodies can never be known by reasoning *a priori*"?

10 The writer of a pamphlet published in 1847 argued that water must be a simple element because "we have the great authority of Aristotle, who states water is one of the four elements", and "chemists are at variance as to the composition of water, for according to Davy water consists of hydrogen and oxygen in the proportion of two parts of the former to one of the latter, whilst Dumas, the celebrated French chemist says that one part of hydrogen and eight parts of oxygen form one of water" What is your opinion about these quotations?

11 In reply to a question asking for the meaning, in words, of the equation $H_2SO_4+Zn=ZnSO_4+H_2$, a candidate said "Two parts of hydrogen (H_2) in sulphuric acid (H_2SO_4) are replaced by one part of zinc (Zn) and zinc sulphate ($ZnSO_4$), with hydrogen gas (H_2) is produced" Criticise this answer, and state how you think it ought to have been expressed

12 The vapour densities of three substances referred to hydrogen taken as unity were 45, 70, and 25 respectively, and the percentages by weight of a certain element contained in each were, 22 22, 42 86, and 40 0 respectively What is the probable value of the atomic weight of the element?—*Cambridge Senr Locals*

Hint The molecular weight of the first element is 90, and it therefore contains 20 parts by weight of the given element, while the second contains 60, and the third 20 parts by weight of the same element Hence, if *A* be the atomic weight of the given element, $uA=20$, $vA=60$, $wA=20$ Hence *A* is probably 20

13 'Valency is the gaseous combining ratio of hydrogen or of other elements to the unit volume of hydrogen, but extended by indirect calculations to those elements whose gaseous volume cannot be directly measured The atomic weight is the weight of a unit volume of the elements in the gaseous condition, compared to that of hydrogen as unity"—*J T Sprague* (1892) Explain this quotation more fully with examples

14 It is said that "if a porous vessel containing a mixture of hydrogen and oxygen in any proportion be surrounded by a vacuum, the mass of oxygen which escapes in a short time is four times that of hydrogen" Expose the fallacy of this statement Hint The effect of partial pressure, which varies according to the relative proportion of the gases present, is ignored

15 In 1703, G Amontons published a paper on "The expansive force of air as a measure of temperature," and showed that the increase of pressure is proportional to the rise of temperature, and also to the increase of density (*a*) Is the latter statement correct? (*b*) If air has a density of 0 00129 (gram per c c) at n.t p, what must be the pressure in order that the density may be three times as great? Hint (*a*) Since volume v varies inversely as density D (p 19), Clapeyron's equation (p 85) can be written $p=RTD$, etc Hence the pressure of a gas is proportional to the temperature and density (*b*) 3 atm

16 A flask fitted with a porous plug contains equal masses of hydrogen and carbon dioxide, and is exposed to the open air until half the hydrogen has passed out Neglecting the changes of diffusion rates due to the varying partial pressure of the gases and also the back action of the air and escaped gases, find the proportion of the two gases remaining in the flask —*R H Jude and H Gossin, Physics*, London, 1899

17 A sealed bottle can stand an internal pressure of four atmospheres and it is filled with a gas at 15° and 760 mm Above what temperature would the bottle be liable to burst?

18 How much zinc and sulphuric acid will be required to fill a cylindrical gas holder 2 metres high and 40 cms diameter with hydrogen gas at n p t? Hint The cubic capacity of the gas holder is $\pi r^2 h$, or 251 2 litres (*i e* cubic decimetres) Hence nearly 1100 grams of sulphuric acid and 730 grams of zinc are needed

19 It is sometimes stated that Avogadro's rule for gases is true for hydrogen and oxygen at ordinary pressures, and hence these gases unite in the proportions 2 1 The researches of Amagat and others on the effects of change of temperature and pressure on the volume of a gas show that hydrogen and oxygen not only deviate from the two gas laws, but their deviations are in opposite directions *Hence, adds A Scott (1887), "it can only be by the merest chance that at our* ordinary temperatures and pressures the combining volumes of hydrogen and oxygen should be exactly 2 1" Discuss this question

20 Is it possible to raise the temperature of a saturated vapour at a constant pressure?

21 "The properties of a compound," said a writer in 1887, "are the sum of those of their components This indeed is a necessity for the atomic theory, which supposes that bodies react in terms of units whose integrity remains inviolate throughout all changes." *Discuss this statement*

22 Describe and explain Soret's experiments on the molecular weight of ozone. If, in Soret's apparatus 100 c c of HCl gas had been mixed with oxygen, and 18 c c had diffused in half an hour, what molecular weight would you assign to an acid gas of which 12 c c (out of 100 c c) diffused under the same conditions?—*Owens Coll*

23 Explain clearly the meaning of the following translation from C L and A B Berthollet's *Élémens de l'art de la teinture*, Paris, 1804 "We may be easily satisfied of the existence of oxygen in chlorine We have only to expose to the light of the sun a phial filled with a solution of chlorine in water Bubbles of gas are soon evolved, and the resulting gas can be collected in a suitable receiver This gas has all the properties of oxygen When the bubbles cease to develop, the liquid has lost its distinctive properties, and it is now water impregnated with ordinary muriatic acid and oxygen."

24 To what constituents do acids owe their characteristic properties? Does this substance impart these properties to all its compounds? What is the theory advanced to explain the facts embraced in your answer? How do we explain the fact that some acids are stronger than others? Name some other facts which the above-mentioned theory explains —*American Coll*

25 Describe the preparation of potassium from potassium carbonate What products are formed when water, moist air, chloric and hydrochloric acid respectively act on potassium? Give an outline of the chemical characters of each of these products —*London Univ*

26 State three definite reasons for placing potassium and sodium in the same class of metals —*Cambridge Senr Locals*

27 A set of silver refining vats have energy equivalent to one horse power applied to them at an average pressure of 3 7 volts per vat How much silver will be deposited per hour? Given 746 watts are equivalent to one horse power Hints Since watts=amperes×volts, the current is 200 amperes, but (p 303) a current which will deposit 0 001118 gram of silver per second is called an ampere, hence 200 amperes will deposit 0 001118×200×60×60=805 grams per hour

28 P A Guye and G Ter Gazarian discovered in 1906 that the most carefully recrystallized potassium chlorate contains at least 0 022 per cent of potassium chloride Taking account of this correction, recalculate the atomic weight of silver from the following data of Stas —Percentage of oxygen in potassium chlorate=39—154, ratio of silver to potassium chloride=100 *69 1143* (O=16) —*Manchester Univ*

29 Describe and explain the changes which take place when nitrogen tetroxide, enclosed in a sealed tube, is heated up Do you know any other gases which undergo similar changes when heated? In what way would you say that electrolytes, when dissolved in water, exhibit an analogous behaviour to nitrogen tetroxide when heated?—*Staffs County School*

30 Describe the changes that take place when the following are heated An aqueous solution of sulphurous acid, an aqueous solution of acid calcium carbonate, an aqueous solution of 40 per cent nitric acid, an aqueous solution of 80 per cent. nitric acid, solid ammonium nitrate, ammonium nitrite, sulphur —*Cape Univ*

31 (*a*) What are the general methods for hastening the rate of a reaction? (*b*) The equation $N_2O_4=2NO_2$ represents a system of two gaseous substances in equilibrium What would be the effect of increasing the pressure on the system without changing the temperature?—*Dept of Educ, Ontario*

32 What is the action of ozone upon potassium iodide, and how would its effect be distinguished from what is produced by nitrogen peroxide upon the same salt? Calculate the weight of potassium iodide which is equivalent to one gram molecule of ozone (K=39 1, I=126 8 O=16) —*Science and Art Dept*

33 Write a general account of the displacement of hydrogen by metals from water, from acids, and from alkalies stating which metals act in this way and which do not What other kinds of action may occur?—*Owens College.*

34. Give in detail practical methods by which *two* of the following bodies may be prepared in a crystalline state hydroxylamine, phosphorus oxide, sodium azoimide, nitrosulphonic acid —*Owens College*

35 When electric sparks are passed through ammonia gas it is nearly all decomposed, when through a mixture of nitrogen and hydrogen a trace of ammonia is formed How can either of these reactions be made practically complete? Explain the reasons for your answer Do you know of any other instances of the same sort of phenomenon?—*Bombay Univ*

36 According to Curtius and Schulz, hydrazine contains 87 4 per cent of nitrogen and 12 6 per cent of hydrogen, and it forms two chlorides, the one contains 26 96 per cent of nitrogen, 6 01 of hydrogen, and 67 41 of chlorine, and the other contains 40 95 per cent of nitrogen, 7 71 of hydrogen, and 51 86 of chlorine What is the molecular formula of hydrazine? J Biehringer, *Einführung in die Stöchiometrie*, Braunschweig, 1900 Hint Take N=14, Cl=35 5, and H=1 The formula for hydrazine, by calculation, is $H_{2n}N_n$, the simplest empirical formula of the first chloride is NH_3Cl, and of the second N_2H_5Cl These numbers show that the first chloride can be regarded as a compound of NH_2 with HCl, and the second chloride a compound of $2NH_2$ with HCl, or the first might be a compound of N_2H_4 with 2HCl, and the second a compound of N_2H_4 with HCl, etc The second suggestion is more probable than the first, because *hydrogen chloride usually behaves in these double compounds as if it were a monad radicle—witness* NH_3 HCl Hence the formulæ of the three compounds in question are respectively written N_2H_4, N_2H_4 2HCl, N_2H_4 HCl Now show that this conclusion is confirmed by the vapour density of hydrazine 1 1 (air=1)

37 By what method is sodium nitrate prepared, and what are its principal uses? How would you obtain from sodium nitrate (*a*) ammonia, (*b*) nitric oxide, (*c*) hydroxylamine sulphate?—*Institute of Chem*

38 How can the nitrides of lithium and magnesium be prepared, and what is the action of water on them? Given the fact that lithium can be obtained by the electrolysis of its fused hydroxide, suggest a continuous process for the conversion of atmospheric nitrogen into ammonium salts —*London Univ*

39 A current passes simultaneously through acidulated water, a solution of copper sulphate, $CuSO_4$, and molten silver chloride What substances are produced in each cell, and how many grams of each in the time that 10 cubic centimetres of hydrogen are liberated from water (Cu=63, Ag=108) ?—*New Zealand Univ*

40 On the assumption that the equivalent of mercury is 99 25, calculate to two places of decimals the equivalents of oxygen, hydrogen, copper, sulphur, and chlorine from the following data mercuric oxide contains 92 59 per cent of mercury, cupric oxide contains 70 9 per cent. of copper, cupric chloride contains 47 3 per cent of copper, sulphuretted hydrogen contains 94 07 per cent of sulphur, hydrogen chloride contains 97 23 per cent of chlorine —*London Univ*

41 Discuss the action of pure nitric acid and of ordinary nitric acid on the metals copper and zinc, and indicate the compounds which are formed respectively under different conditions —*Board of Educ.*

42 Compare and contrast the physical and chemical properties of magnesium with those of calcium and zinc To which of these two metals do you consider magnesium to be more closely related ? Give reasons for your answer Given a solution containing these three metals, how would you prepare from it pure specimens of the oxides of each ?—*Oxford Univ*

43 Calculate the weight of oxygen available for oxidation in 10 grams of potassium of permanganate in sulphuric acid solution —*Sheffield Scientific School, U S A*

44 How can crystallized potassium permanganate be obtained from black oxide of manganese ? Explain the reactions which ensue when an acidified solution of potassium permanganate interacts with (*a*) sulphurous acid, (*b*) oxalic acid, (c) hydrogen peroxide —*Sheffield Univ*

45 What weight of manganese dioxide must be decomposed by hydrogen chloride in order to obtain enough chlorine to combine completely with the hydrogen evolved by dissolving 10 grams of magnesium in dilute acid ? (Mg=24, Mn=55, Cl=35 5, H=1) —*Vic Univ Manchester*

46 Represent by equations the action of strong sulphuric acid on each of the following substances (*a*) nitre, (*b*) manganese dioxide, (*c*) formic acid, (*d*) copper, (*e*) charcoal

47 The properties of an element depend in a great measure on the different active valencies of the element Illustrate this principle by reference to manganese

48 Describe the difficulties to be overcome in determining whether N_2O_3 is formed when NO and NO_2 are mixed at ordinary temperatures What conclusions have been drawn from the results of experiments on this problem ?—*Board of Educ*

49 Describe, with all essential practical details, the preparation *either* of pure crystallized sodium nitrate from sodium nitrate, or of pure potassium perchlorate from potassium chlorate What method would you adopt to ascertain the purity of the product ?—*Board of Educ*

50 State Dulong and Petit's law and explain its value in the determination of atomic weights If the specific heats of two metals M and N be 0 25 and 0 214, and their equivalents 12 and 9 respectively, what will be the formula of their chlorides ?—*Sheffield Univ*

51 Give the composition of "pure air" by weight and by volume Give proofs that the air is a mechanical mixture It is intended to prepare 112 litres of nitrogen, at S T and S P, from a certain chemical compound, what compound will it be best to employ, and how many grams will be required ?—*Princetown Univ U S A*

52 By what experiments and reasoning has it been shown that air is a mixture of gases ? By whom and how was the active constituent of air first isolated, and the nature of combustion explained ?—*Sheffield Univ*

53 Beginning with nitrogen combined in the form of nitre, state exactly how you would prepare from it (*a*) nitric oxide, (*b*) nitrous oxide, (*c*) ammonia, (*d*) nitrogen, each in a state of purity —*London Univ*

54 A certain metal gave the following results (i) 0 5 gram gave 1 396 grams of oxide, (ii) the chloride contained 11 2 per cent of the metal, (iii) the vapour density of the chlorine was found to be 40, (iv) the specific heat at ordinary temperatures was 0 46, but increased rapidly with rise of temperature State what you can about the atomic weight of the metal.—*Oxford Univ*

55 Explain the terms "atomic heat" and "molecular heat" The specific heat of lead sulphate, $PbSO_4$, is 0 0827, that of lead 0 0309, and of sulphur 0 163 Assuming the atomic weights of lead and sulphur to be 207 1 and 32 07 respectively, calculate the specific heat of solid oxygen Give a short account of the attempts which have been made to find a common value of the atomic heat for all elements in the solid state —*Board of Educ.*

56 The equivalent of carbon in methane is 3, in ethylene 6, in acetylene 12 On what considerations is the atomic weight of carbon fixed as 12?—*St Andrews Univ*

57 How would you distinguish between (*a*) a soluble iodide and a soluble bromide, (*b*) graphite and iodine, (*c*) nitrous oxide and oxygen, (*d*) a ferrous and a ferric salt? Give equations —*St Andrews Univ*

58 Describe the methods adopted and the results obtained in the study of the limited oxidation of methane and its homologues —*Board of Educ*

59 Sketch the history of the recognition of the property of "radioactivity," and give an account of the isolation of radium salts Describe exactly with diagrams how you would investigate the nature of the radiation from a given mineral —*Board of Educ*

60 Give a short account of the metallic ammines What is known regarding their constitution?—*St Andrews Univ*

61 Write a brief essay on valency, taking into account the existence of "molecular" compounds —*London Univ*

62 Give an account of the principal ammoniacal bases or ammines containing cobalt or platinum, and explain Werner's theory of their constitution —*Board of Education*

63 Platinum chloride was added to a solution of ammonium chloride, and the resulting precipitate, after ignition, left 1 7 grams of platinum What weight of ammonium chloride was present in the solution? (Pt=195, N=14, H=1, Cl=35 5)—*Board of Educ*

64 Give the formulæ of the following substances, state whether each is soluble or insoluble in water, and suggest pairs of solutions which would give the insoluble substances as precipitates (*a*) calcium chloride, (*b*) barium carbonate, (*c*) aluminium hydroxide, (*d*) phosphorus chloride, (*e*) phosphoric chloride, (*f*) copper sulphide, (*g*) ammonium sulphate, (*h*) strontium nitrate —*Univ Toronto*

65 Describe two experimental proofs of each of the following statements (*a*) the oxygen, nitrogen, and carbon dioxide in the atmosphere are not chemically combined, (*b*) the oxygen, nitrogen, and hydrogen in nitric acid are chemically combined —*Cambridge Senior Locals*

66 State exactly how you would separately prepare from phosphorus specimens of phosphorous acid, orthophosphoric acid, and hypophosphorous acid How may these acids be recognized qualitatively? What structural formula would you ascribe to orthophosphoric acid, and for what reasons?—*Institute of Chem*

67 If the structural formula of phosphorous acid be correctly represented by $P{=}(OH)_3$, how would you expect this acid to decompose on heating?

68 What reactions take place when (*a*) silver nitrate solution is acted upon by (i) arseniuretted hydrogen, (ii) antimoniuretted hydrogen, and (iii) chlorine, (*b*) when sulphuretted hydrogen acts on ferric chloride solution, and (*c*) when solutions of the following are brought in contact (1) silver nitrate and sodium phosphate, (2) potassium iodide and copper sulphate, (3) ferrous sulphate and nitric acid?—*Cape Univ*

69 Give examples of monatomic, diatomic, triatomic, and tetratomic molecules of elementary substances, and state how their construction has been arrived at —*Science and Art Dept*

70 What are the natural sources of arsenic? Describe how the element is obtained from its ores, and mention some of the uses to which arsenic and its compounds are put How could you test a specimen of iron pyrites for arsenic?—*Cambridge Univ*

71 Discuss the action of zinc on aqueous solutions of the following sodium hydroxide, nitrous acid, sulphurous acid, cupric chloride, arsenic acid?—*Institute of Chem*

72 Describe and explain the changes which take place in the following experiments (*a*) carbon dioxide is passed into lime water, (*b*) chlorine is passed into water containing mercuric oxide in suspension, (*c*) sulphurous acid gas is passed

into a solution of iodine, (d) sulphurous acid gas is passed into a solution of hydrogen iodate, (e) potassium permanganate solution is added to a solution of hydrogen peroxide in dilute sulphuric acid, (f) phosphorus is boiled with baryta water —*Owens Coll*

73 On what experimental evidence is it believed that acids, bases, and salts are more or less ionized in aqueous solution? Explain from this point of view (a) the alkalinity of a sodium carbonate solution, (b) the acidity of a ferric chloride solution, (c) the action of ammonium chloride in preventing the precipitation of magnesium salts by ammonia?—*Madras Univ*

74 Coal gas of the composition given below is burnt in air —

H_2	CH_4	C_2H_2	C_2H_6	C_6H_6	CO	CO_2	CS_2	N_2	
48 0,	26 0,	2 0,	3 0,	1 0,	15 0,	2 0,	0 1,	2 7	per cent

Name the products, and give the quantities of each produced per litre at N T P of gas burnt, stating your results in c c measured at 100° and 760 mm —*Institute of Chem*

75 Describe an electrolytic method for preparing sodium Show how the modern applications of electrolysis have (a) aided in the production of cyanides, (b) reduced the profits of the Leblanc soda process, (c) aided in the production of bleaching liquids —*Cape Univ*

76 In 1813 Davy wrote "I have given an account of an experiment on the combustion of potassium in silicated fluoric acid gas" (SiF_4), "in which the gas was absorbed, and a fawn coloured substance formed, which effervesced with water, and left, after its action on that fluid, a residuum which burnt when heated with oxygen, reproducing silicated fluoric acid gas, and I concluded from the phenomena that the acid gas was decomposed in the process, that oxygen was probably separated from it by potassium, and that the combustible substance was a compound of the siliceous and fluoric bases" Elucidate, as far as you can, what happened in the experiment described, and comment upon Davy's explanation of it, and on the terminology he uses —*Owens Coll*

77 Pieces of bright metallic lead are placed (a) in distilled water, (b) dilute hydrochloric acid, (c) dilute sulphuric acid, (d) water saturated with carbon dioxide, (e) a chalk water of about 15° hardness, give an account of the changes which you would expect to observe or be able to trace —*Institute of Chem*

78 Each of the following substances is heated in a stream of hydrogen PbO, SnO_2, Fe_2O_3, TiO_2, Cr_2O_3, Mn_3O_4, Al_2O_3, P_2O_5, B_2O_3, ZnO, BaO State what occurs in each case, giving equations —*Institute of Chem*

79 What is the effect of heat on the following substances arsenic acid, phosphorus pentachloride, lead nitrate, auric chloride, lead dioxide?—*London Univ*

80 What happens when the following substances are warmed with concentrated nitric acid tin, antimony, aluminium, arsenious oxide, phosphorus, hydrogen chloride, ammonia?—*London Univ*

81 A graduated gas cylinder is supported vertically in a mercury trough so that the upper end of the tube is distant a mm from the level of the mercury, and the level of the mercury inside the cylinder is distant b mm from the outside level. The tube must be expressed c mm in order to make the level of the mercury inside and outside the same What is the pressure of the atmosphere outside? If the height of the tube from the level of the mercury is 300 mm, the difference in the levels of the mercury in the two vessels, 152 mm, and the levels of mercury inside and outside are the same when the tube is depressed 187 6 mm, show that the height of the barometer is 760 mm *Answer* $b(a-b)/(c-3)$

82 Show that a deviation from the law of persistence of weight would be inconsistent with the law of persistence of energy *Hint* If an atom of weight w, when combining with another atom of weight w' does not produce a molecule of weight $w + w'$, and the weight of the molecule be greater than that of the two constituent atoms, it would suffice to let the molecule fall some convenient distance, and raise this again while the atoms are uncombined to gain a little energy

83 On heating strongly 0 406 gram of potassium chlorate, 139 c c of oxygen were obtained, and the potassium chloride remaining weighed 0 247 gram The oxygen was measured over water at a temperature of 27°, at which temperature the vapour pressure of water is 2 66 cm The barometric height was 71 14 cm. Find the value for the molecular weight of oxygen which may be deduced from these data

84 Explain the following quotation "When the term 'salt' is used in every

day life, it refers naturally to sodium chloride, but to a chemist a salt may not only be a chloride, but a sulphide, a sulphate, or one of a number of similar compounds "—W Segerblom, *First Year Chemistry*, Exeter, 1909

85 T Thomson (*A System of Chemistry*, London, 1817) said "The atomic theory seems to me to present an insuperable objection to the opinion advocated by Berthollet, that *mass* produces an effect upon chemical combinations and decompositions " Show that there is no difficulty in reconciling Berthollet's generalization (p 97) with Dalton's atomic theory

86 To what constituents do acids owe their characteristic properties? Does this substance impart these properties to all its compounds? What is the theory advanced to explain the facts embraced in your answer? How do we explain the fact that some acids are stronger than others? Name some other facts which the above mentioned theory explains —*American Coll*

87 State, with explanations, how electrolytes differ from non electrolytes as regards the depression of freezing point or the osmotic pressure exerted by equimolecular solutions, and explain how the degree of ionization of a salt in solution might be calculated from a determination of osmotic pressure *a* grams of a non-electrolyte are made up to 100 c.c. with water at 15° C The osmotic pressure is found to be 500 mm Express in factors the molecular weight of the substance —*Cape Univ*

88 What is the difference between the chemical equivalent and the electro chemical equivalent? (*a*) The chemical equivalents of zinc, aluminium, and (ferrous) iron are respectively 32 5 9, and 28 What are the respective electrochemical equivalents of the elements? Distinguish between "unit quantity of electricity" and "unit current of electricity" (*b*) How many units of current will deposit 0 01118 grm of silver per minute? *Answers* (*a*) The electro chemical equivalent of zinc is 32 5, aluminium 9, and ferrous iron 28, the electro chemical equivalents in coulombs are respectively 0 00034, 0 000095, and 0 00029 (*b*) $\frac{1}{6}$ amp

89 The durability of galvanized iron is, under ordinary circumstances, much greater than that of tin plates (iron coated with tin) Explain this —*New Zealand Univ*

90 If hydrogen sulphide be pressed into a mixture of iodine and water, sulphur is deposited and hydrogen iodide is formed, the iodine may be in turn displaced from combination by bromine, and the bromine by chlorine What weight of each of these elements would be required to displace the sulphur contained in 100 grms of hydrogen sulphide? ($S = 32$, $I = 127$, $Br = 80$, $Cl = 35\ 5$) —*London Univ*

91 What do you understand by positive ions, negative ions, and complex ions? Give examples Give examples of metals (two at least in each case) (*a*) which form more than one simple positive ion, (*b*) which form only one oxide or hydroxide, and this oxide or hydroxide, although usually giving a simple positive ion, sometimes forms part of a negative ion, (*c*) which form more than one oxide, and in certain salts form part of a negative ion; (*d*) which in some parts form part of a complex positive ion Give the formula of the ion in each case —*Sydney Univ*

92 The analysis of a potassium hydrogen arsenomolybdate by C Friedheim (1892) gave the following data 0 4328 grm analyzed for potash gave 0 1138 grm of platinum, for arsenic 0 78819 grm of substance gave 0 3418 grm $Mg_2P_2O_7$, 0 5038 grm weighed 0 0587 grm after ignition The MoO_3 was determined by difference Show that these numbers correspond with 12 67 per cent of K_2O_5, 32 41 per cent of As_2O_5, 11 65 per cent H_2O, and 43 27 per cent MoO_3, and hence agree with the formula $K_2O\ As_2O_5\ 2MoO_3\ 5H_2O$

93 The element manganese is commonly classed as a metal Point out how this is justified There are however, some compounds of manganese, the study of which would lead to its classification with other elements certainly not metals. Give an account of any of these you can, and say what comparisons they suggest to you

94 When 0 2041 grm of anhydrous ferrous chloride was exposed to ammonia gas at 18 52°, H Wolfram (1913) found that 235 1 c c. were absorbed Barometer 746 mm Show that this very nearly corresponds with the formation of $FeCl_2\ 6NH_3$

95 Show that the heat of formation of phosphorus nitride, P_3N_5, from red phosphorus is nearly 70·4 *cals*, given the heats of combustion of the nitride P_3N_5 to nitrogen and phosphorus pentoxide is 474 7 cals, and of red phosphorus 370·8

cals; and further, that the heat of formation of the nitride from colourless phosphorus is 81 5 cals, given the heat of combustion of colourless phosphorus 370 8 cals

96 C Rammelsberg (1841) analyzed a crystalline salt obtained by treating antimony pentasulphide with concentrated potassium hydroxide, and found K, 23 40, Sb, 37 80, S, 18 19, O, 7 30, water, 13 30, and he considered these numbers agreed satisfactorily with the formula $K_3SbS_4\,KSbO_3\,5H_2O$ Is the formula in accord with the observed data? Show that the theory for the formula requires K, 23 00, Sb, 37 86, S, 18 89, O, 7 04, H_2O, 13 20, a sufficiently close approximation

97 Discuss the subject of the luminosity of flame, and account for the fact that compressed hydrogen and oxyen burn with luminosity, also that when the mixed gases are exploded in a confined space the flash is luminous What recently ascertained fact proves that a hydrocarbon flame contains glowing particles of solid matter?—*Science and Art Dept*

98 Calculate the composition of a gas from the following analytical data —

Original volume of gas in burette		100 c c
Remainder after treatment with caustic potash		94 6 c c
„ „ „	potassium pyrogallate	94 6 c c.
„ „ „	cuprous chloride	70 6 c c.
Half of the residual gas was expelled, leaving		35 3 c.c
Air was added, making a volume of		87 3 c c
After combustion		76 1 c c.

City and Guilds London Inst

Hint 100 – 94 6 = 5 4 c c CO_2, oxygen *nil* (p 562), 94 6 – 70 6 = 24 0 c c CO (p 682), 87 3 – 76 1 = 11 2, and $(11\ 2 \times \frac{2}{3}) \times 2 = 14\ 92$ c c hydrogen, 100 – (5 4 + 240 + 14 92) = 55 68 c c of nitrogen

99 In the determination of the composition of a sample of gas by Hempel's burette, the following results were obtained From the data given calculate the percentage of the gas —

Gas taken		100 c c
After absorption	by caustic potash	93 3 c c
„ „	by potassium pyrogallate	98 0 c c
„ „	fuming H_2SO_4	93 9 c c
„ „	cuprous chloride	87 8 c c

20 c c of the gas were then transferred to the burette, and 46 c c of air added, and the mixture passed over palladiumized asbestos The volume after combustion was 50 5 c c to 50 5 c c of gas, 22 c c of oxygen were added the mixture exploded, and the CO_2 absorbed by caustic potash The volume after explosion was 54 5 c c, and after the absorption of CO_2, 45 5 c.c —*City and Guilds London Inst*

Answer 1 7 per cent CO_2, 0 3 oxygen (p 562), 4 1 olefines, etc (p 696), 0 1, CO (p 682), 20 + 46 = 66, 66 – 50 5 = 15 5, $15\ 5 \times \frac{2}{3} = 10\ 3$ c c per 20 c c of gas, $\frac{1}{20}$ of $10\ 3 \times 87\ 8 = 45\ 21$ per cent of hydrogen (p 693), 54 5 – 45 5=90 c c of CO_2, equivalent to 9 0 c c CH_4 per 20 c c of gas, $\frac{1}{20}$ of $9 \times 87\ 8 = 39\ 5$ per cent of CH_4

100 Compare the cost of obtaining 1000 Cals of heat by electricity at 1*d* per kilowatt hour, of oil fuel at ½*d* per kilogram (per 8790 Cals), and of coal gas at ⅛*d* per cubic metre (per 5000 Cals) *Hint* One kilowatt hour is equivalent to 864 Cals (p 572) Hence the cost of electricity is to that of oil fuel is to that of coal gas as 1 172 0 0282 0 025*d*

101 Give in detail practical methods by which two of the following bodies may be prepared in a crystalline state hydroxylamine, phosphorus oxide, sodium azoimide, nitrosulphonic acid —*Owens Coll*

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THE END

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